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PULP AND PAPER

Chemistry and Chemical Technology

VOLUME II:
Properties of Paper
and Converting

① Paper – Properties
② Pulp – nature & type -

PULP AND PAPER
Chemistry and Chemical Technology

IN TWO VOLUMES

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VOLUME II:
Properties of Paper and Converting

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PREFACE

to Volume II

Volume I of this book was concerned with the chemistry of the basic pulp and papermaking operations, such as pulping, bleaching, stock preparation, sheet formation, filling, sizing, and coloring. The properties of paper and the important paper-converting operations are discussed in this volume. These converting operations include pigment coating, printing, coating with resins and waxes, saturation of paper with resins and waxes, and laminating—operations that are closely related to papermaking. They are often carried out in the same plant where the paper is made and, in fact, there is an increasing trend toward carrying out these operations directly on the paper machine as an integral part of the papermaking process. Converting operations are so inextricably tied in with the fundamental properties of paper that they cannot be discussed without a thorough knowledge of paper chemistry. By the same token, satisfactory paper for converting operations cannot be made without a knowledge of the basic requirements of these operations. For these reasons, it is highly desirable that the paper chemist understand the various converting operations. Many paper chemists are engaged in technical service work and have to follow their company's products into converting plants during times of trouble, or when experimental work is being carried out. This requires a special knowledge of these fields which should be a part of every paper chemist's training. It is with these ideas in mind that the chapters on paper-converting processes have been written.

The author received considerable aid in writing this part of the book, and the names of those who helped in this work are listed in the preface to Volume I. To them, the author again wishes to express his appreciation.

J.P.C.

Decatur, Illinois
April, 1952

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CHAPTER XVI

PROPERTIES OF PAPER

Although all papers are made from essentially the same raw materials, there is considerable variation in the properties of commercial papers. The purpose of this chapter is to discuss the significance of the common paper properties and to discuss the relationship between these properties and the use requirements of the paper.

Introduction to Paper Testing

The characteristics of paper are divided into physical, optical, chemical, electrical, and microscopical properties. Physical properties include thickness, weight, density, hardness, stiffness, and tensile strength. Optical properties include light transmittance, light absorption, and light reflectance. Chemical properties include *p*H, moisture content, alpha cellulose, and copper number. Electrical properties include dielectric strength, specific inductive capacity, and electrical conductivity. Most of the important properties of paper are discussed in this chapter, although certain properties are discussed in other chapters; for example, wetting properties are discussed in the chapter on sizing, and water vapor resistance is discussed in the chapter on coating with resinous materials.

Any listing of tests used on paper would be incomplete without mention of the handling tests in which the paper is tested for such properties as feel, rattle, snap, and look-through. These tests have been widely used in the past, and even though physical measurements have replaced them to a large extent, considerable paper is still purchased on the basis of these tests. Handle, according to Strachan,[1] is a sense impression of bulk, regularity of flatness and finish, and resistance to bending under the paper's own weight. An experienced papermaker can obtain considerable information about the paper from handling, but this information cannot be expressed by numerical values. Hence, the paper industry and paper-consuming industries are rapidly adopting technical standards. In most cases, however, standard samples are furnished with each order to which the delivery must conform in finish, color, and formation.

Certain tests made on paper are primarily use tests which are based on the element of utility. These tests simulate actual conditions to which the paper may be subjected in use and are generally very complicated in nature. They include such tests as the proof press testing of printing papers, coating of rawstock and testing of the coated paper, and laminating of papers on small laboratory laminating machines. Another example is the measurement of water vapor resistance on boxboard after fabrication in the form of the finished package so that it is possible to obtain over-all information on the creasing, folding, handling, and sealing properties of the paper. The fabrication and testing of corrugated paperboard is another example. This involves engineering problems which are at least as important as the physical properties of the paperboard; for example, the scoring and creasing of the paper has a tremendous influence on the over-all strength of the box. Although there is a correlation between the strength of the original paperboard and the strength of the finished corrugated box, corrugated paperboard manufacturers place most of their reliance on tests made on the finished box, often after it is filled. Compression resistance, deflection at maximum compression, resistance to wear in the revolving drum tester, and other similar tests are among those commonly made on the finished box. The advantage of "use" tests is that they furnish information on the utility of the paper for a particular purpose. Their disadvantage lies in the inability to express results in generally understood terms and in their lack of relationship with other tests.

---

[1] J. Strachan, *Paper-Maker 113,* No. 2: 9–11 (Feb., 1947)

Types of Properties Measured

Most of the commonly used tests for measuring paper properties are arbitrary tests. Arbitrary tests are those which are dependent upon arbitrary instrument design and carefully defined procedure as to size of sample and other variables. Such tests generally measure a complex property of the paper which is a combination of several fundamental properties. Because of their complex nature, results based on arbitrary tests are difficult to relate to the papermaking operations unless the person making the test has had considerable experience.

Fundamental tests, on the other hand, give basic information about the structure of the paper which is capable of better correlation with the papermaking operations. Fundamental properties are independent of dimensions, procedures, or instrument design, and hence can be mathematically related to other fundamental properties. There is an increasing interest in the use of fundamental tests for analyzing paper properties, but so far, very few such tests are in use. The advantage of these tests is that once the fundamental characteristics are thoroughly understood, it should be possible to predict the utility of the paper for any purpose.

Effect of Papermaking Variables on Properties of Paper

Most paper properties are dependent upon the fact that the basic constituent is cellulose. These are called functional properties.[2] Examples of functional properties are the ability of paper to "wet" readily with water, and the tendency of paper to lose strength when wet. Functional properties cannot be changed without chemical treatment of the fibers or protection of the paper through saturation or coating.

---

[2] R. H. Mosher and R. J. Bracewell, *Paper Trade J. 122,* No. 16: 172–174 (Apr. 18, 1946)

The type of wood used, the extent of cooking and bleaching, and the degree of bonding between fibers determine, to a large degree, the physical and optical properties of the paper. The amount of fiber treatment, formation on the wire, amount of wet pressing, method of drying, and amount of calendering are the principal factors affecting the degree of bonding. These variables must be controlled to obtain a finished paper of the desired properties, which often means sacrificing one property to another. For example, envelope papers, which require toughness, folding resistance, good writing surface, good printing surface, and high opacity, are made in such a way as to sacrifice some toughness and folding endurance in order to obtain the desired opacity. The amount and type of sizing agent, filler, and coating material applied to the paper affects the properties, as has been shown in previous chapters.

Sampling and Conditioning Paper

Before any tests can be carried out, it is necessary to obtain samples which are representative of the material to be tested. Paper is no exception to this rule, and the old adage that a test is no better than the sample is as true for paper as it is for other materials. The methods of sampling pulp and paper products have been fully described in TAPPI Standards, and will not be repeated here.[3] The theory of sampling is discussed in Chapter XVII.

Once representative samples have been obtained, they should be protected from anything which will change their properties, which means that they should be protected from excess heat and light and not be allowed to come into contact with liquids. Paper should be handled as little as possible, particularly when optical tests are to be made, since fingerprints affect many of the properties. No tests should ever be made on areas containing watermarks, creases or other visible imperfections in the paper.

Light has relatively little effect on paper, unless the paper is aged for a long period of time. Moisture content, on the other hand, has a very pronounced effect on the properties of paper, particularly the physical and electrical properties, and is one of the most important factors affecting the performance of paper in use, as well as during the period of test. Paper testing should be carried out in a room maintained at constant temperature (usually 73 ± 3.5° F.) and constant relative humidity (usually 50 ± 2%).[4]

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[3] *The Manufacture of Pulp and Paper*, Vol. V, McGraw-Hill Book Co., New York, N. Y. (1929)

[4] In England and France, 65% relative humidity and 65 to 70° F. are used.

The time of conditioning should be sufficient to bring the paper to a uniform moisture content, which usually requires from four to twelve hours, although certain treated papers and heavy paperboard may require twenty-four to forty-eight hours. Paper should not be subjected to very high humidity before conditioning, since this alters the sheet structure irreversibly, affecting all the physical properties and certain of the optical properties, such as gloss.[5] For very accurate work, where the hysteresis in equilibrium moisture is important, paper should be preseasoned for at least two hours at a low humidity (e.g., 35% relative humidity) before the regular conditioning period. After the test specimens are properly conditioned, they should be handled as little as possible and not breathed upon.

Temperature has relatively little effect on the physical, chemical, and optical properties of paper within the range normally encountered. However, temperature does affect some of the physical properties, e.g., differences in temperature of 1° C. cause a change in folding endurance of about 3% in the case of bond and ledger papers and temperature influences the moisture content of paper, even at constant relative humidity, so that it is best to control the temperature during the testing of paper. Paper moved from a cold atmosphere into a warm atmosphere (as, for instance, when paper is moved from a cold warehouse into a warm converting plant) is subjected to a higher humidity than that which prevails in the rest of the room because of the cooling effect of the paper on the air in the immediate surroundings. This condition exists as long as a temperature difference exists between the paper and the atmosphere. The effective relative humidity under these conditions can be determined from special charts.[6] A rough approximation suitable for cases where only a slight temperature difference exists can be made on the basis that a 1° F. temperature difference changes the effective relative humidity by 2%.

Wire and Felt Sides

Paper has two sides, the wire and the felt sides. The wire side is almost always the rougher because of the diamond-shaped pattern caused by wire marks. Paper is generally open or porous on the wire side, and closed or non-porous on the felt side. This difference in smoothness and porosity on the two sides of paper is referred to as two-sidedness.

The difference in texture between the wire and felt sides is generally visible to the naked eye if the paper is folded over and the two surfaces compared directly. If not readily visible, the paper can be submerged in water or dilute sodium hydroxide solution for a few seconds, blotted, and then examined as above. This loosens the fiber structure and tends to overcome the smoothing effect of calendering. Another test is to dry a strip of paper in an oven and note the direction of curl, which is usually toward the wire side. An experienced person can distinguish between the felt and wire sides by tearing first with the wire side uppermost, and then with the felt side uppermost. A more feathered edge is obtained when the wire side is uppermost. Examining a strip of paper taken from the fold tester just before the strip breaks will usually differentiate between the two sides of the paper, since the sheet will generally appear more worn on the felt side than on the wire side.

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[5] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 104*, No. 15: (Apr. 15, 1937)

[6] TAPPI Data Sheets

Certain physical and optical tests are customarily made on both the wire and felt sides, or if only one side is tested, the side used is specified. Wire and felt sides should always be taken into account in the use of paper. In the case of forms to be printed on one side only, best results are obtained by printing on the felt side. When laminating high-quality papers, *e.g.*, bristols, it is customary to put the wire sides together in order to keep the smoother felt sides on the outside.

Many papers are watermarked by means of a dandy roll which presses upon the sheet in the wet condition, thereby leaving the sheet thinner in the outline of the design. In some cases, the dandy roll is covered with fine wire similar to the machine wire which produces an impression similar to that on the wire side of the sheet. This paper is referred to as a "wove" paper because it has the same surface on both sides, just as it would have if the sheet had been woven.

Machine and Cross Direction

Paper has a definite grain caused by the greater orientation of fibers in the direction of travel of the paper machine and the greater tension exerted on the paper in this direction. This is known as the machine direction. The cross direction is the direction of the paper at right angles to the machine direction.

The grain of paper must be taken into account in measuring all physical properties. In measuring tensile strength, folding endurance, and tearing resistance, strips of paper are cut in both directions in order to measure the strength in both the machine and cross directions. The tensile and folding strengths are greater in the machine direction than in the cross direction, whereas the tearing resistance is greater across the machine direction. The grain of the paper must be taken into account in measuring optical properties of the paper, such as brightness and gloss.

Papers vary in their ratio of machine to cross direction strengths. Cylinder-machine papers have a higher ratio of machine-to-cross-direction strength than Fourdrinier papers. However, even Fourdrinier papers generally have from 1.5 to 2.0 times as high tensile strength in the machine direction as in the cross direction. Orientation in the machine direction of Fourdrinier papers is very marked on the bottom (wire) side of the sheet, and distinctly less on the top (felt) side. Steenberg and Danielsen[7] found (by adding a small percentage of colored fibers to the stock) that the number of fibers lined up in the machine direction on the wire side is about 10 times greater than the number lined up in the cross direction. On the felt side, however, the number of fibers in different directions is roughly the same, except in the close vicinity of the machine direction, where there are twice as many fibers as in the other directions. This is shown in Figure XVI-1, where the results of fiber counting are given in polar coordinates.

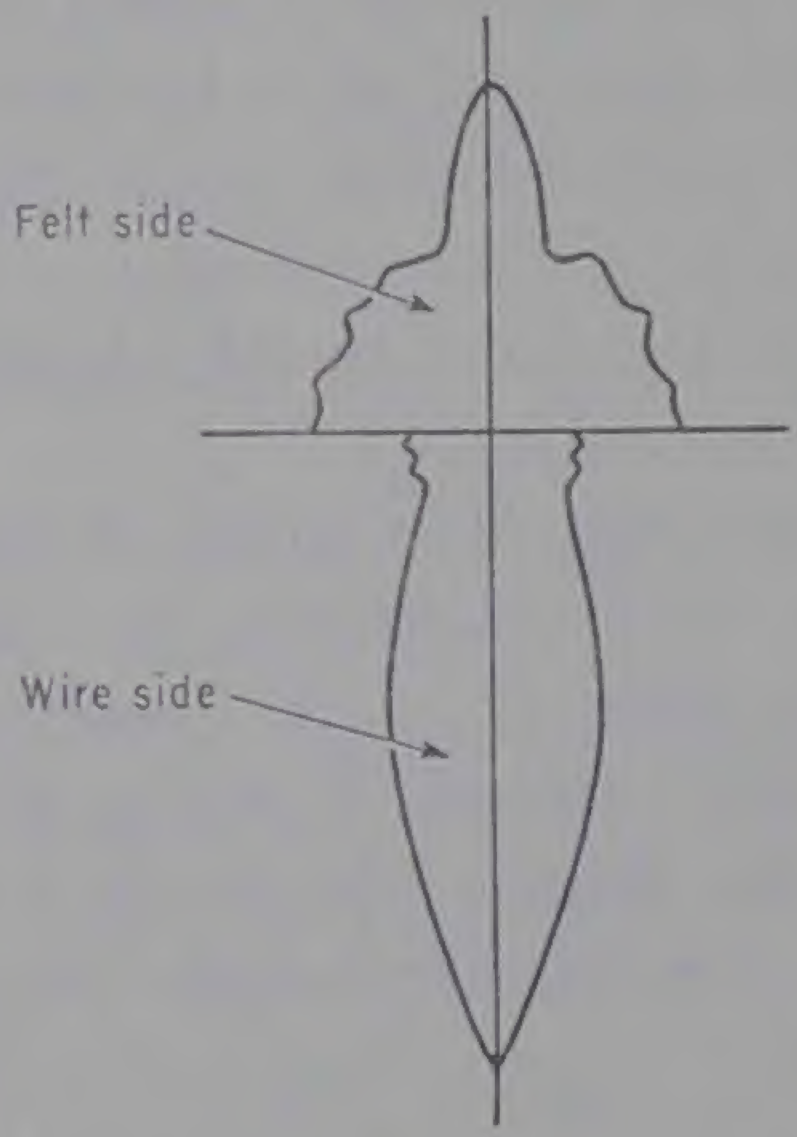

Fig. XVI-1. Fiber distribution in polar coordinates for machine and cross directions (160 g./m.^{2}).

The length of an arrow from the center of the figure to the curve gives a measure of the number of fibers lying in that position.

Machine conditions during paper manufacture have a very definite effect on the ratio of machine to cross direction strength. The important factors have already been discussed in the chapter on sheet formation (Ch. VIII), and in general, they include the amount of "shake" on the machine, the velocity of the stock in relation to the wire speed, and to a great extent the amount of tension applied to the wet sheet.

Ordinarily there is less variation in paper properties in the machine direction than in the cross direction, because variations occur slowly in the machine direction, whereas in the cross direction they may occur quite suddenly, on account of uneven flow of stock on the wire, uneven wet pressing, or uneven tension during drying. Moreover, there is a normal variation in cross direction strength of the paper, depending upon how far the sample was taken from the edge of the sheet.

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[7] R. Danielsen and B. Steenberg, *Svensk Papperstidn. 50,* No. 13: 301–305 (July 15, 1947)

There are several means of determining machine and cross directions of paper. Some of the methods are as follows:

(*1*) By visual observation, since with most papers it is possible to see that more fibers are lined up in the machine direction. The longer diagonal of the wire mark is always lined up in the machine direction.

(*2*) By wetting one surface of a small square of the specimen and noting the axis of curl, which is always parallel to the machine direction. The curl is due to the fact that the water causes the under side of the sheet to expand, and since the sheet tends to expand more in the cross direction than the machine direction, this forces the sheet to form a cylinder whose axis is parallel to the machine direction.

(*3*) By cutting two narrow strips (6 × ½ in.) in both directions of the sheet and noting the stiffness in the two directions. The machine direction stiffness of thin paper is much greater than the cross direction stiffness, and this can be detected in a stiffness tester or by holding the two strips in one hand and noting which one bends more.

(*4*) By noting the way in which the sheet "pops" when bursting strength is measured. This test is based upon the fact that paper has less stretch in the machine direction than in the cross direction. Thus, when pressure is exerted by the rubber diaphragm of the bursting strength tester, the sheet expands readily in the cross direction; but since it cannot expand appreciably in the machine direction, it bursts suddenly and with the longest rupture in a line at right angles to the machine direction.

(*5*) By measuring the tensile strength or folding endurance in both directions. Strips cut parallel to the machine direction will usually show a greater tensile strength and folding endurance than strips cut in the cross direction.

(*6*) On thin papers made on a cylinder machine, it is possible to distinguish between machine and cross direction by tearing the sheet in both directions and noting the direction of tear. The line of tear tends to turn so that it is parallel to the machine direction, since the resistance to tear is less in this direction.

Most papers are made with machine direction and cross direction strength as nearly equal as possible. There are exceptions, however, where it is desirable to have maximum tensile strength in the machine direction (e.g., cable wrapping papers and twisting papers). All papers should be used to take the greatest advantage of the grain of the paper. As pointed out in Chapter XIX, it is desirable to cut printing papers with the machine direction in the longer direction and to feed the sheet to the press with the machine direction parallel to the axis of the press roll. Diazotype papers are also cut with the machine direction in the long direction. Book paper folds better and the book stays open better if the sheets are cut so that the machine direction runs up and down the page. In making tabulating cards, it is desirable to cut the sheet with the machine direction upright in order to take advantage of the greater stiffness in this direction. In laminating paper plys, it is sometimes desirable to place alternate layers of paper with their cross and machine directions at right angles to each other, although this is not always practical. Wrap-around labels for metal cans are generally cut with the machine direction vertical to obtain the greatest flexibility about the can.

Physical Properties

Paper is a self-supporting, structural material. It is not an end in itself, since nearly all paper is used as a base for coatings or printing inks, or used as a wrapping or packaging material, where a strong, well-constructed material is required. Paper resembles other structural materials, such as glass, wood, and metals, in that it possesses tensile strength, elasticity, and strength modulus in bending. However, by convention, tensile strength, elasticity, and strength modulus are not measured directly in paper testing, but instead empirical tests are used. These tests measure the durability of the paper and its resistance to applied force. The manner of applying the force varies with each paper-testing instrument.

Basis Weight

Weight is the most common specification made on paper, because most paper is sold on a weight basis. Weight of paper is expressed per unit of area, rather than per unit of volume, as is the case with most other materials, because paper is used in sheet form and area is more important than volume. The consumer who buys paper by the roll or ream is concerned about the weight of the paper which he has purchased, because paper which is heavier than specified will give fewer sheets than paper of standard weight, whereas paper which is lighter than specified will give a greater number of sheets, but these will be lacking in thickness, strength, and opacity. The manufacturer may be inclined to make a somewhat heavier paper than specified, but the user is interested in buying the lightest paper which is suitable for the purpose. Paper which is only slightly overweight can mean a substantial economic loss to the paper consumer. It is customary to bill at the ordered weight unless the paper is excessively underweight, in which case the paper is billed at the scale weight. Tolerances are generally allowed in basis weight and quantity ordered.

The common unit for expressing the weight of paper in the English system is the number of pounds of paper per ream, a ream representing either 480, 500, or, in the case of United States Government Printing Office, 1,000 sheets. In the metric system, the weight is expressed as the number of grams per square meter of paper (1,550 sq. in.). It is obvious how much confusion would arise if the weights of different papers were expressed in all the various trade sizes used. To prevent such confusion, trade custom has established certain basic sizes which are used as a standard for expressing weights in the different grades of paper. The basic ream sizes for the various paper grades are given in Table I.

TABLE I

BASIC REAM SIZES

Grade of paper	Ream size, in.	Number of sheets in ream
Book and offset papers	25 × 38	500
Blotting	19 × 24	500
Bristols	22½ × 28½	500
Box cover	20 × 24	500
Cover	20 × 26	500
Manuscript cover	18 × 31	500
Cover	20 × 26	1000
Index bristol	25½ × 30½	500
Tag and mill bristol	22½ × 28½	500
News	24 × 36	500
Bond, writing, ledger, and manifold	17 × 22	500
Hanging, waxing, wrapping, and tissue	24 × 36	480
Tissue (optional)	20 × 30	480

Reasons for the various basic ream sizes can be traced to the sizes established in the early days of papermaking as the most satisfactory for printing, folding, and trimming paper of that grade. For example, the basic size of bonds (17 × 22) is just four times the common size used in most business stationery (8½ × 11) and the basic size of book papers (25 × 38) is sixteen times the common size used in book formats (6 × 9) when allowance is made for trimming.

It should be emphasized that a particular grade of paper is not necessarily cut and sold in the basic ream size. The various grades of paper are stocked and sold in many different sizes, depending upon what different mills have found to be necessary in the handling of their business. There is considerable variation in the sizes used, but paper trade associations and the Government Printing Office have succeeded in simplifying and standardizing on certain sizes. For example, the Writing Paper Manufacturers' Association has adopted seven standard or trade sizes for bond papers as follows: 17 × 22 (basic size), 17 × 28, 19 × 24, 22 × 34, 24 × 38, 28 × 34, and 34 × 44. The Government Printing Office uses eleven standard sizes for uncoated book paper: 22½ × 35, 24 × 36, 25 × 38 (basic size), 28 × 42, 28 × 44, 30½ × 41, 32 × 44, 33 × 44, 35 × 45, 36 × 48, and 38 × 50. Other grades of paper have their own customary trade sizes. Considerable interest has been manifested in the adoption of a single basic ream, size 25 × 40 and 1,000 sheets, in order to simplify the computation of weights on odd sizes of paper. This standard size is widely used in technical work, but is not used to any extent in commercial work.

Basis weight is the term used in the industry to refer to the weight in pounds of a ream containing either 480, 500, or 1,000 sheets cut to a given

TABLE II

Conversion Factors for Converting Ream Weight from One Basis Weight to the Other

Weight	Grams/ sq.m.	Pounds										Lb./1,000 sq.ft.
		17 × 22 —500	22½ × 28½ —500	22 × 34 —500 or 17 × 22 —1000	24 × 36 —500	24 × 36 —480	24 × 37 —500	25 × 38 —500	25 × 40 —500	30 × 40 —500	25 × 40 —1000	
Grams/sq.m.	1.000	0.266	0.456	0.532	0.614	0.590	0.631	0.676	0.711	0.853	1.423	0.205
Pounds												
17 × 22—500	3.759	1.000	1.715	2.000	2.311	2.219	2.374	2.541	2.675	3.209	5.348	0.770
22½ × 28½—500	2.193	0.583	1.000	1.166	1.347	1.293	1.385	1.471	1.560	1.871	3.119	0.449
22 × 34—500 17 × 22—1,000	1.880	0.500	0.857	1.000	1.155	1.109	1.187	1.270	1.337	1.604	2.674	0.385
24 × 36—500	1.627	0.433	0.742	0.866	1.000	0.960	1.028	1.100	1.158	1.389	2.315	0.333
24 × 36—480	1.695	0.451	0.773	0.902	1.041	1.000	1.070	1.145	1.206	1.447	2.411	0.347
24 × 37—500	1.583	0.421	0.722	0.842	0.973	0.934	1.000	1.070	1.126	1.351	2.252	0.324
25 × 38—500	1.480	0.394	0.675	0.787	0.909	0.873	0.935	1.000	1.052	1.263	2.105	0.303
25 × 40—500	1.406	0.374	0.641	0.748	0.864	0.829	0.888	0.950	1.000	1.200	2.000	0.288
30 × 40—500	1.172	0.312	0.534	0.623	0.720	0.691	0.740	0.792	0.833	1.000	1.667	0.240
25 × 40—1,000	0.703	0.187	0.321	0.374	0.432	0.415	0.444	0.475	0.500	0.600	1.000	0.144
Pounds/1,000 sq.ft.	4.882	1.299	2.226	2.597	3.000	2.880	3.083	3.298	3.472	4.167	6.944	1.000

size, which is usually the basic ream size. The basis weight of container boards is generally calculated as the weight per 1,000 sq.ft., whereas the basis weight of boxboards is generally figured at the basic size of 25 × 40—1000. The basis weight of commercial papers varies, depending upon the grade of paper, use to which the paper is to be put, and the demands of the user. Standard weights established by the Government Printing Office for different grades of paper are as follows:

Bond: 13, 16, 20, and 24 lb.
Ledger: 24, 28, 32, 36, 40, and 44 lb.
Machine-finish book: 30, 35, 40, 50, 60, and 70 lb.
Supercalendered book: 40, 50, 60, and 70 lb.
Coated book: 50, 60, 70, and 80 lb.

Government Printing Office weights are usually expressed on the basis of a 1,000-sheet ream, but the above is expressed on a 500-sheet ream to conform to general usage. The weight of writing papers is sometimes expressed as substance number, that is, the weight of a ream 17 × 22—500 (basic size for writing papers). Table II gives conversion factors for converting ream weight from one basic size to the other.[8] To convert from ream weight in the left-hand column to basis shown in the other column, multiply the ream weight by the factor given in the other column.

Ream weight is measured on a specially graduated scale which may be a beam quadrant type (Thwing), or quadrant of the pendulum type (Schopper, Cady), or the lever type (Toledo). The scale gives a direct reading in pounds which is 480 or 500 times the actual weight of the sample. In the case of the Thwing, a small weight is added or withdrawn from the scale, depending upon whether a 500- or a 480-sheet reading is desired. Because of the way the scale is constructed, every error is multiplied by either 480 or 500 times, and consequently the scale should be set up where it is not subject to air currents. The pointer can be adjusted for zero, and the scale can be adjusted for sensitivity by using appropriate weight adjustments. The scale should be checked against check weights from time to time. The check weight should give a reading on the scale in pounds per 500 sheets equal to the check weight in grams multiplied by 1.102 (500/454). In the case of 480 sheets, the reading in pounds should equal the check weight multiplied by 1.058 (480/454). Differential scales having two baskets may be used in the case of coated or impregnated papers. A sheet of the untreated paper and the treated paper, both having the same dimensions, are placed in the two baskets of the scale so that the scale indicates directly the weight per ream of material applied in treating the paper. In the case of the lever type (Toledo) scale, there are two or three scales which record automatically the weight of 480, 500, or 1,000 sheets. If the weight per 1,000 sq.ft.

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[8] TAPPI Data Sheets

of stock is desired, a sample cut exactly 1 ft. square can be used and the weight read directly from the 1,000-sheet scale.

In weighing paper at the mill, it is customary to use samples which have been cut accurately to the proper ream size so that the basis weight may be read directly from the scale. For routine testing, templates are used for cutting the samples which are usually one-half or one-quarter the ream size so that the sample sheet taken from the reel must be folded twice or four times. If a sheet of odd size is used, the following relationship can be used:

$$\text{weight in ream size desired} = \text{weight of sample} \times \frac{\text{area of ream size desired}}{\text{area of sample weighed}}$$

This same formula can be used for converting from one ream size to another when the additional factor below is used:

$$\frac{\text{number of sheets in ream desired}}{\text{number of sheets in known ream}}$$

When only small samples are available, it is better to weigh on an analytical balance and convert the reading by means of the following relationship:

$$\text{weight in ream size desired} = \text{weight of sample in grams} \times (1.102) \times \frac{\text{ream size desired}}{\text{length} \times \text{width of sample in inches}} \times \frac{\text{number of sheets in ream size desired}}{500}$$

This formula is based upon the conversion of grams per single sheet to pounds for 500 sheets, using the factor 1.102 (500 × 0.0022046 lb./g.).

For best results, paper should be weighed only after it has been conditioned under standard conditions of relative humidity (50%) and temperature (73° F.), since paper gains or loses moisture with changes in the humidity and temperature. Extreme variations in humidity such as occur between seasons can result in a substantial change in weight. If a constant humidity room is not available for testing paper, it is possible to make approximate conversions for the effect of humidity on weight by using Table III which shows the percentage of the weight on the scale which should be subtracted or added to convert to the proper weight at 50% relative humidity.[9]

An interesting new device for measuring the basis weight of paper continuously and automatically is the beta-ray basis weight gage.[10,11] This device consists of a fixed arrangement of a suitable radioisotope and a detector between which the paper passes as it leaves the last calender stack. The paper absorbs beta rays in direct proportion to its mass so that the response

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[9] "Facts about Paper Testing," No. 4907, Thwing-Albert Instrument Co., Philadelphia, Pennsylvania (1949)

[10] E. A. Crawford and M. Strain, *Tappi 33,* No. 4: 190–192 (Apr., 1950)

[11] A. P. Schreiber, *Tappi 33,* No. 6: 28A, 30A, 34A (June, 1950)

TABLE III

CORRECTIONS OF BASIS WEIGHT FOR HUMIDITY

Add or subtract the following percentage from the weight shown on the scale

Relative humidity, %	Alpha cellulose and rag papers	Average papers	Groundwood papers
20	+1.5	+2.5	+3.3
30	+1.0	+2.0	+2.7
40	+0.5	+1.0	+1.3
50	0.0	0.0	0.0
60	−0.5	−0.7	−1.2
65	−1.0	−1.5	−2.2
70	−1.7	−2.5	−3.7
75	−2.5	−4.0	−5.2
80	−3.5	−5.0	−7.2

of the detector to the rays passing through the paper is a function of the basis weight.

Weight affects all the physical properties of paper and many of the optical and electrical properties. It is customary to report physical properties such as bursting strength and tensile strength in terms of weight; for example, bursting strength is often expressed as "points" per pound, which is obtained by dividing the bursting strength in pounds per square inch by the basis weight in pounds per ream. Optical properties, on the other hand, are generally reported on the paper as is, without any correction for weight. The ratio of strength to weight varies with the weight of the paper; in general, the highest strength in relation to weight is obtained on papers lighter than 35 lb. per ream.[12] There has always been a demand for strong, lightweight paper, and the demand has become greater with the advent of air mail and air transportation.

Thickness

Thickness of paper is measured in a micrometer as the distance between two circular plane surfaces (about ¼ in. in diameter) under a pressure of 8 to 9 p.s.i. The results are reported in thousandths or ten-thousandths of an inch. In the case of paperboard, the term "points" is used for each 0.001 in. of thickness; for example, paperboard 0.030 in. in thickness is referred to as 30-point board. The thickness reading is affected by the moisture content of the paper and the pressure used in the micrometer.

Thickness affects nearly every physical, optical, and electrical property of paper. It is highly important in the case of filing cards, which should not exceed the required thickness to avoid taking up valuable space in the filing cabinet. Tabulating cards must be made to an accurately controlled thickness in order to function properly in tabulating machines which are adjusted for exact feeding and sorting of the cards. Thickness is important in the case of book papers, since it affects the opacity of the paper and the amount of impression received on the printing press. Thickness is a factor in the performance of condenser papers, blotting papers, saturating papers, wrapping papers, and many other grades. The thickness gage tends to measure only the thickest part of the paper because of the relatively large diameter of the micrometer (about ¼ in.). For some uses, variations in thickness not measurable with ordinary micrometers are of considerable significance.

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[12] G. K. Dickerman, *Paper Trade J. 118*, No. 26: 239–242 (June 29, 1944)

Density

The true density of paper is probably the most important fundamental paper property. Density is related to the porosity, rigidity, hardness, and strength of the paper, and, in fact, density influences every optical and physical property except sheet weight. Because of its fundamental nature, sheet density has been suggested as the most satisfactory basis for comparing the strength and other properties of different papers.[13]

The specific gravity of paper cannot be determined by the customary method of water displacement, and hence it is more appropriate to speak of the density of paper. Density is commonly calculated by dividing the basis weight of the paper by the caliper, but since the value obtained in this way depends upon the ream size used, the result should be termed apparent density. According to the A.S.T.M. method, density is determined as follows:

$$\text{density} = \frac{\text{weight in grams per square meter} \times 0.0001001}{\text{thickness in centimeters}}$$

Specific volume is often used in place of density; it is calculated as follows:

$$\text{specific volume} = \frac{\text{thickness in microns (0.001 mm.)}}{\text{basis weight in grams per square meter}}$$

$$= \frac{\text{thickness in mils}}{\underset{(25\times 40\text{—}500)}{\text{basis weight in pounds}}} \times 18.08$$

Specific volume is the volume in cubic centimeters occupied by 1 g. of paper under an applied pressure of about 9 lb. per square inch. Density is the reciprocal of specific volume.

There are two types of density, density (bulk) which is obtained as a ratio of the weight to the thickness of the finished paper, and density which is obtained as the weight of the paper to the thickness before the paper is finished to remove surface irregularities. The difference between these two densities is determined by the difference in smoothness between the uncalendered and calendered paper.

The density of the final paper is controlled by the type of fiber, amount of beating, degree of water removal on the wire, amount of wet pressing, and the amount of calendering. Data by Clark[14] shows that the dry apparent density of groundwood test sheets is accurately linearly proportional to the logarithm of the amount of beating over most of the beating range. Other factors affecting density are the amount of fiber debris, the fineness and flexibility of the fibers, and the hemicellulose content of the pulp.[13] The effect of different pulps on the sheet density is almost a specific property. Sulfate pulps produce sheets of greater density than sulfite pulps. Soda pulps produce sheets of very low density and are used for their bulking properties.

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[13] J. d'A. Clark, *Paper Trade J. 116,* No. 1: 1–8 (Jan. 7, 1943)

Rosin, fillers, and other non-fibrous materials affect the density of paper (fillers being particularly important). The presence of these materials in the sheet changes the density from the true density of the fibrous portion.

For a given basis weight and sheet thickness there can be but one density. Doughty[15] has made three variable plots showing the weight, thickness, and solid fraction for several commercial grades of paper, for some of which the approximate ranges are given in Table IV. Clark[16] gives values of specific volume for several different papers, as shown in Table V. The amount of air space in different papers varies from about 60 to 70% by volume for bulky papers to about 15 to 25% by volume for high-density papers. Baird and Irubesky[17] list the per cent air by volume for several grades of paper, as shown in Table VI.

TABLE IV

APPROXIMATE RANGES OF WEIGHT, THICKNESS, AND SOLID FRACTION FOR SEVERAL COMMERCIAL PAPERS

Type of paper	Basis weight, lb., 24 × 36—500	Thickness, 0.001 in.	Solid fraction
Glassine	18– 45	1.0– 2.8	0.62–0.75
Bond, writing, S.C. book	30– 70	2.5– 6.0	0.45–0.65
Cement bag	75–120	9.0–25.0	0.20–0.45

TABLE V

SPECIFIC VOLUME OF SEVERAL GRADES OF PAPER

Type of paper	Specific volume
Bulky groundwood paper	3.0
Unbeaten sulfite paper	1.8
Glassine	1.0
Cellulose	0.65

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[14] J. d'A. Clark, *Paper Trade J. 110*, No. 9: 121–124 (Feb. 29, 1940)
[15] R. H. Doughty, *Paper Trade J. 95*, No. 10: 111–118 (Sept. 8, 1932)
[16] J. d'A. Clark, *Paper Trade J. 110*, No. 9: 121–124 (Feb. 29, 1940)
[17] P. K. Baird and C. E. Irubesky, *Tech. Assoc. Papers 13*, 274–277 (May, 1930)

TABLE VI

PER CENT AIR BY VOLUME IN SEVERAL GRADES OF PAPER

Type of paper	Air, %
Groundwood	63.1
News	53.1
Greaseproof	43.2
Bond	34.2
Glassine	13.0

The increase in tensile strength obtained as a result of increased beating can be attributed to an increase in the density of the paper brought about by an increase in the area of fiber contact. Clark[18] found that burst and tensile strength are linearly proportional to density, whereas tear (after a certain maximum) is inversely proportional to density. Porosity is inversely proportional to density, as shown in Figure XVI-2, where the effect of solid fraction on the porosity of spruce sulfite pulp is shown for three different fractions of the pulp.[19] Density greatly affects the optical properties, particularly the opacity (see Figure XVI-29).

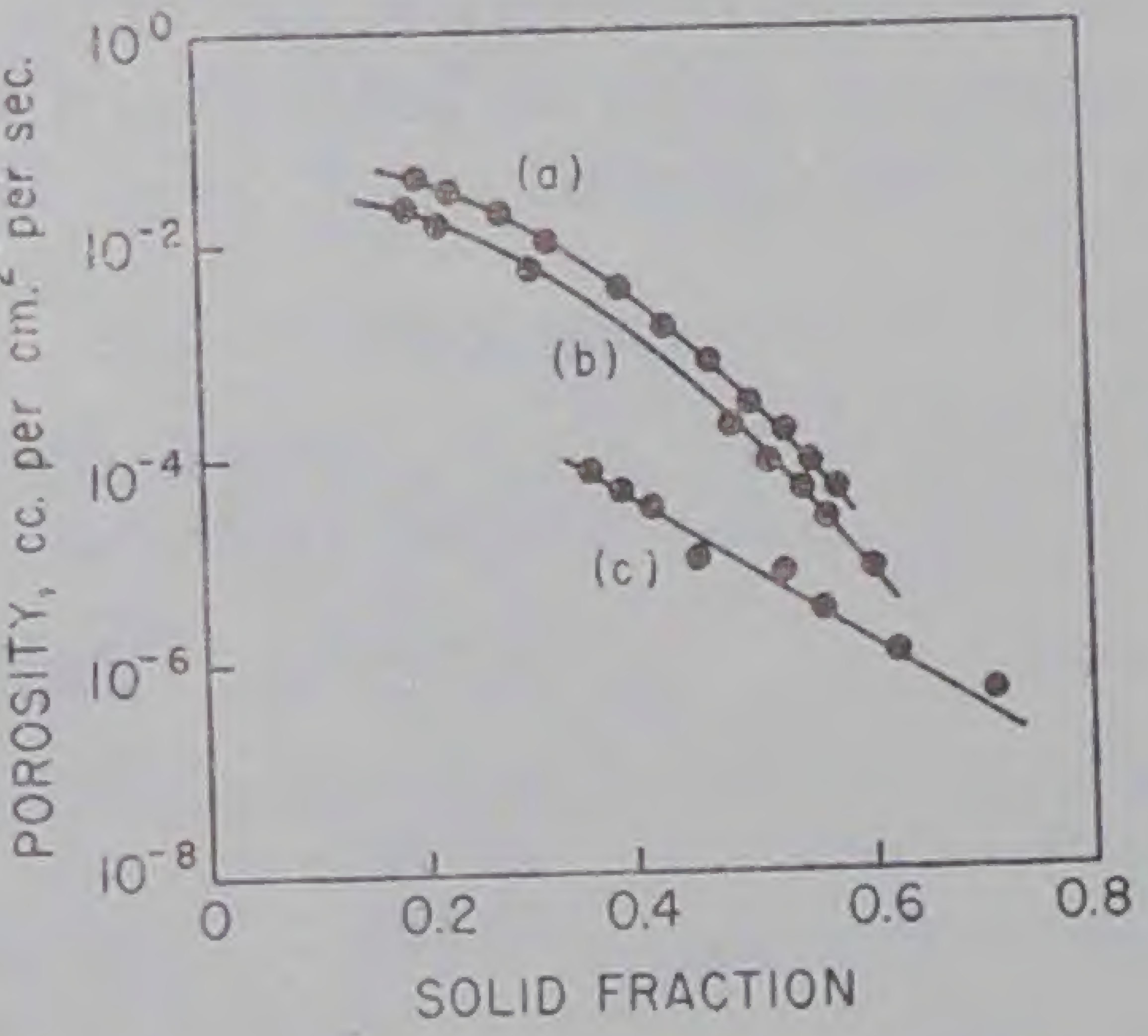

Fig. XVI-2. Relationship between porosity (rate of air transmission) and solid fraction for various fractions of spruce sulfite pulp: (a) long fraction; (b) whole pulp; (c) short fraction.

As strong evidence of the fundamental nature of density, Doughty[20] was able to show that papers of the same solid fraction have the same tensile strength when the same pulp is used, and that papers of constant weight show a mathematically regular increase in tensile strength with increase in solid fraction.[21] Increased beating (after a slight amount) has no effect on tensile strength so long as the solid fraction is held constant. Figure XVI-3 shows the effect of solid fraction on tear, burst, fold, and tensile when unbeaten spruce sulfite pulp is made into sheets of different solid fraction by variation in the amount of wet pressing. The results are similar to those obtained when the solid fraction is varied by different degrees of beating. The modulus of rupture of fiberboards prepared from semichemical pulps has been shown[22] to be directly related to the square of the specific gravity of the fiberboards, as shown in Figure XVI-4.

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[18] J. d'A. Clark, *Pulp Paper Mag. Canada 44,* No. 1: 92–102, Convention Issue (1943)

[19] R. H. Doughty, *Paper Trade J. 95,* No. 10: 111–118 (Sept. 8, 1932)

[20] R. H. Doughty, *Paper Trade J. 94,* No. 9: 114–119 (Mar. 3, 1932)

[21] R. H. Doughty, *Paper Trade J. 93,* No. 15: 162–167, 172 (Oct. 8, 1941)

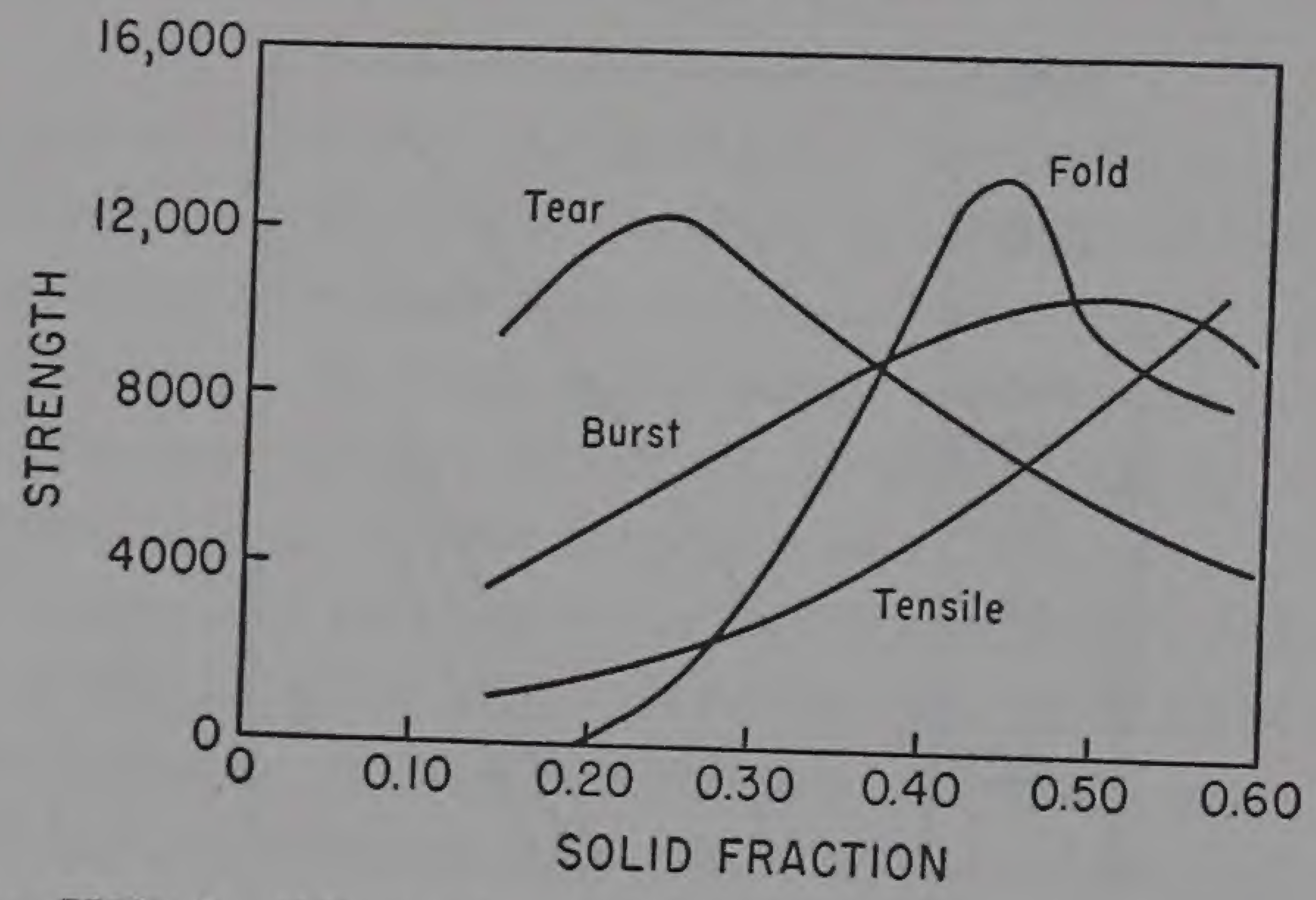

Fig. XVI-3. Effect of solid fraction obtained by wet pressing on physical properties of paper (unbeaten spruce sulfite). Burst in points per pound per ream × 10,000. Tear in grams per pound per ream × 5,000. Tensile in pounds per square inch. Fold × 10.

The above results do not mean that density is an absolute indication of sheet strength when comparing different pulps. That this is not the case has been shown by Doughty[23] who found that papers made from the whole pulp (gum) were stronger at the same solid fraction than papers made from either the fines or the long-fibered fraction. Moreover when all other conditions are equal, long-fibered (coniferous) pulps generally produce papers of higher tensile strength for a given density than short-fibered (hardwood) pulps, which is illustrated by the data in Table VII, obtained by Doughty.

There are cases when the density of the paper can be increased without proportionately increasing the bursting and tensile strength, even when the same pulp is used. Calendering relatively dry paper, for example, tends to increase the (apparent) density without proportionately increasing the burst and tensile strength. Cobb and coworkers[24] found that the addition of starch to the furnish will, in some cases, increase the strength without proportionately increasing the density. Fillers increase the density but decrease strength, but in this case the solid fraction (or density) of the fibrous material is lower for the filled paper than for the paper unfilled for a given thickness and basis weight.

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[22] H. D. Turner, J. P. Hohf and S. L. Schwartz, *Paper Trade J. 127*, No. 9: 43–50 (Aug. 26, 1948)

[23] R. H. Doughty, *Paper Trade J. 94*, No. 9: 114–119 (Mar. 3, 1932)

[24] R. M. Cobb, D. V. Lowe, E. Pohl and W. Weiss, *Paper Trade J. 105*, No. 7: 105–108 (Aug. 12, 1937)

A density measurement on paper gives valuable information about the paper when taken in conjunction with the strength properties. For example, if a paper has a high burst and a low density, the chances are that it is made from long-fibered, tough stock, whereas paper which has a high burst and a very high density is probably made from short-fibered, well-hydrated stock.[25] In the latter case, the sheet will have lower tearing and folding strength compared with the paper made from the long-fibered stock.

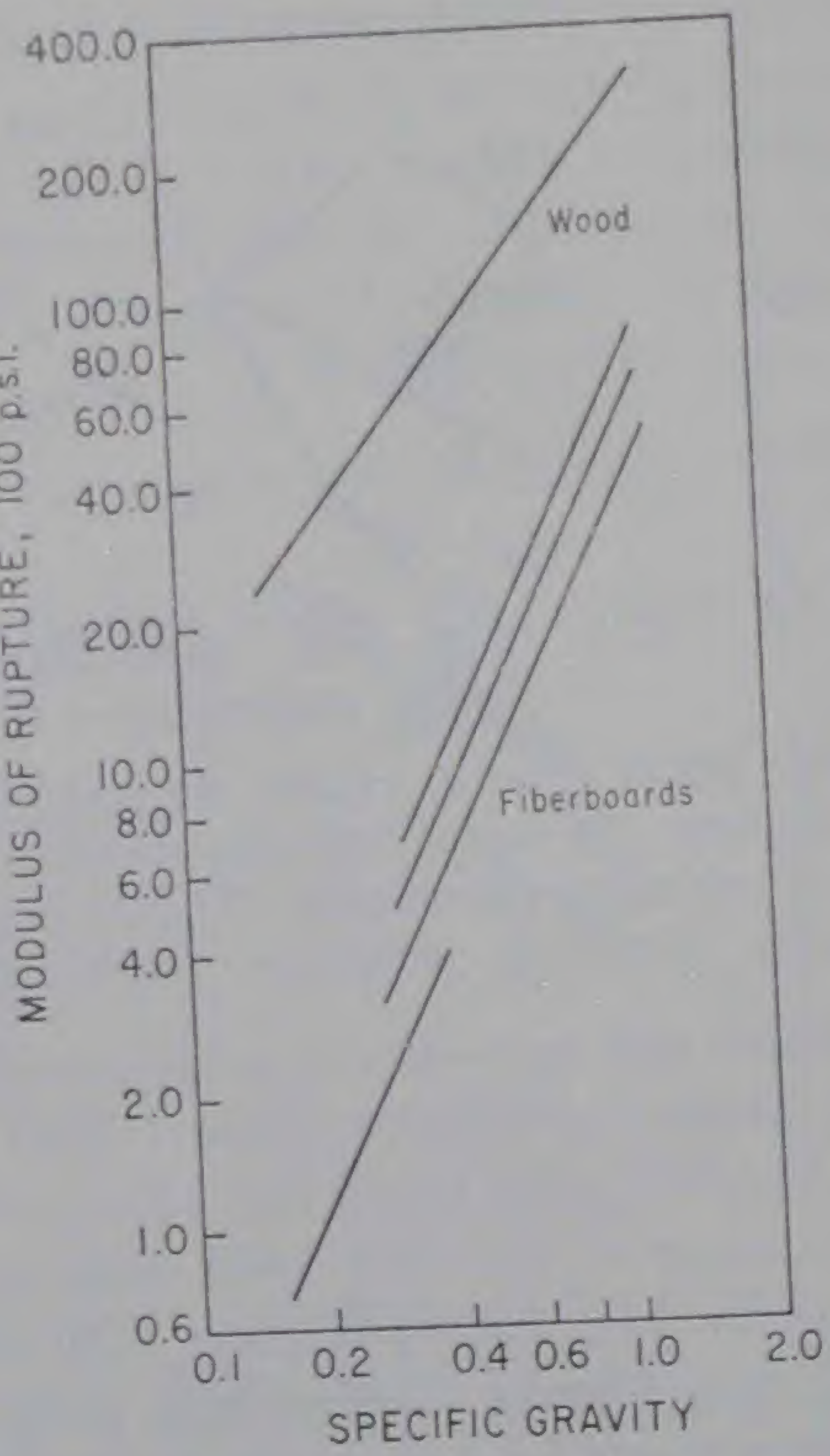

Fig. XVI-4. Effect of specific gravity on modulus of rupture of fiberboards.

Stress-Strain Relationships of Paper

Recently there has been considerable interest in fundamental studies of paper strength based upon stress-strain relationships. These studies have provided an understanding of the nature of paper strength and have helped in the interpretation of other more common tests.

Paper strength is a vague term which means nothing unless the use to

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[25] J. d'A. Clark, *Paper Trade J. 104,* No. 8: 118–120 (Feb. 25, 1937)

TABLE VII

RELATION OF TENSILE STRENGTH (POUNDS PER SQUARE INCH) TO SOLID FRACTION FOR BLACK GUM AND SPRUCE PULPS

Solid fraction	black gum sulfite pounds per square inch	spruce sulfite pounds per square inch
0.20	500	800
0.30	1150	2000
0.40	2250	3500
0.50	3900	5500

which the paper is to be put and particular strength property desired are carefully specified. Paper is not necessarily weaker in the cross direction than in the machine direction merely because the tensile strength is lower in the cross direction. In some ways, paper is stronger in the cross direction than it is in the machine direction, as evidenced by the fact that the paper breaks first in the machine direction when tested in the Mullen tester. It is illogical to speak of paper strength without careful definition, just as it is illogical to compare glass and rubber for strength without denoting the strength characteristics to which reference is made, since glass has high static strength and poor impact strength, whereas rubber has very little static strength but good impact properties. Certain papers require high static strength (e.g., index bristols), whereas other papers require high impact strength (e.g., bag papers).

Before discussing stress-strain relationships, it is desirable to define what is meant by stress, strain, ideal elastic solids, and ideal liquids. Stress is the internal force per unit of area (dynes per square centimeter or pounds per square inch) which resists the external load. Strain is the ratio of the change in dimensions to the original dimensions. Ideal elastic solids are those which deform instantaneously under applied load to a degree linearly proportional to the load and return to their original dimensions when the load is removed. The maximum stress which the specimen will bear and still return to its original shape is called the elastic limit.

Time is not a factor in elastic solids, but it is a factor to be considered in fluids, since ideal liquids exhibit flow, which is dependent upon time as well as upon load. Paper, like many other solids, exhibits both elastic properties and time-dependent flow properties, which means that the stress developed in producing a particular strain will vary with the time involved in producing the strain. Rance[26] has illustrated the time dependence of the stress-strain relationships of paper by testing uniform specimens of paper, first in a Schopper tensile tester and then by hanging various weights onto strips of the paper. The samples tested in the tensile tester had an average breaking load of 10 kg. (involving a time of applied load of about 4 seconds).

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[26] H. F. Rance, *Paper-Maker*, Midsummer Number 22–32, 49, 50, 51 (1949)

This would indicate that the tensile strength is 10 kg., but when a load of 9 kg. was applied, the strip broke, only this time eleven minutes were required. Upon continued testing, it was found that the strip would break under a load of 8 kg. in a period of fourteen hours, and under a load of 4 kg. in a period of 220 days. It should be emphasized that both the elastic properties and flow properties of paper are important in the use of the

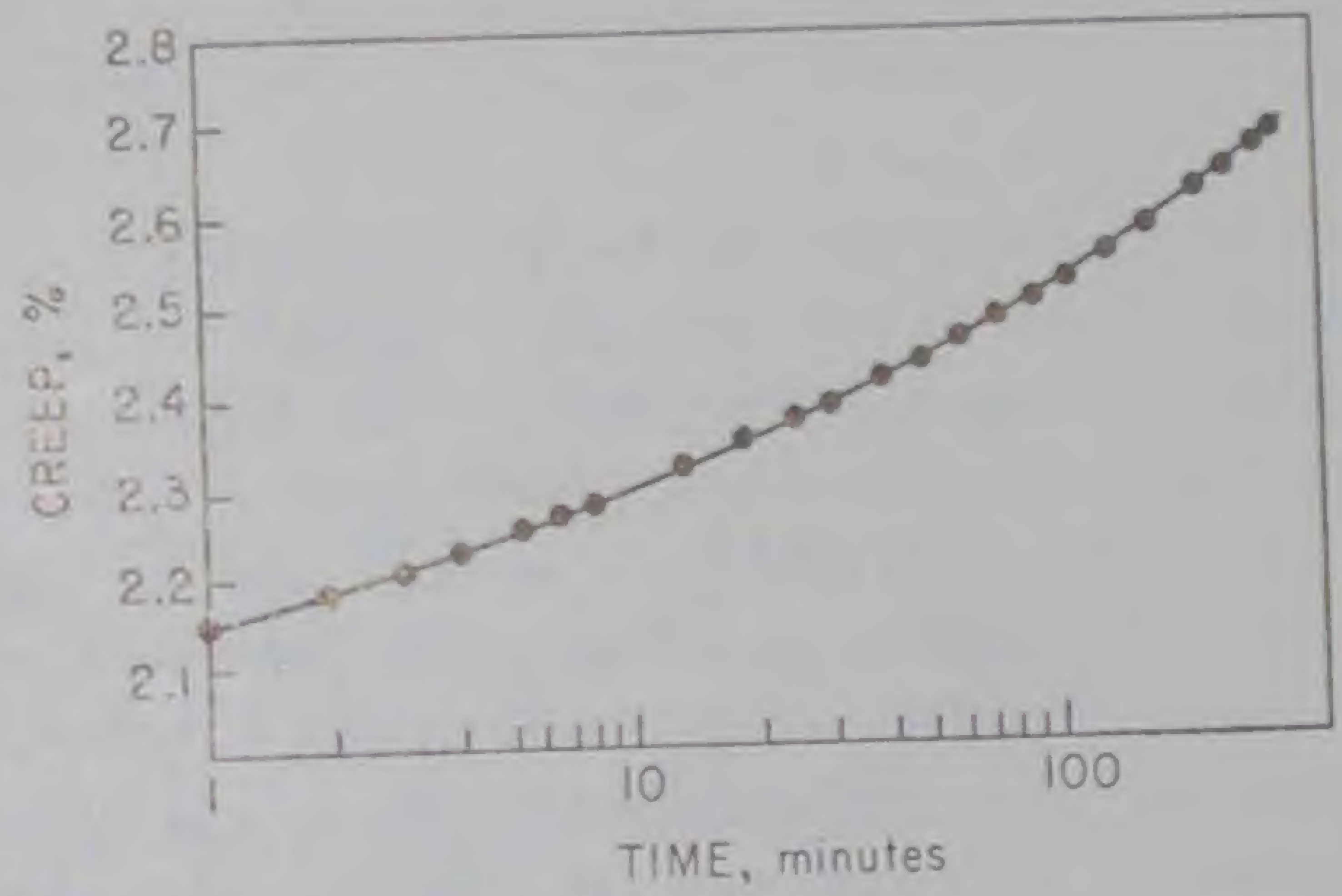

Fig. XVI-5. Creep of paper with time under 75% of breaking load.

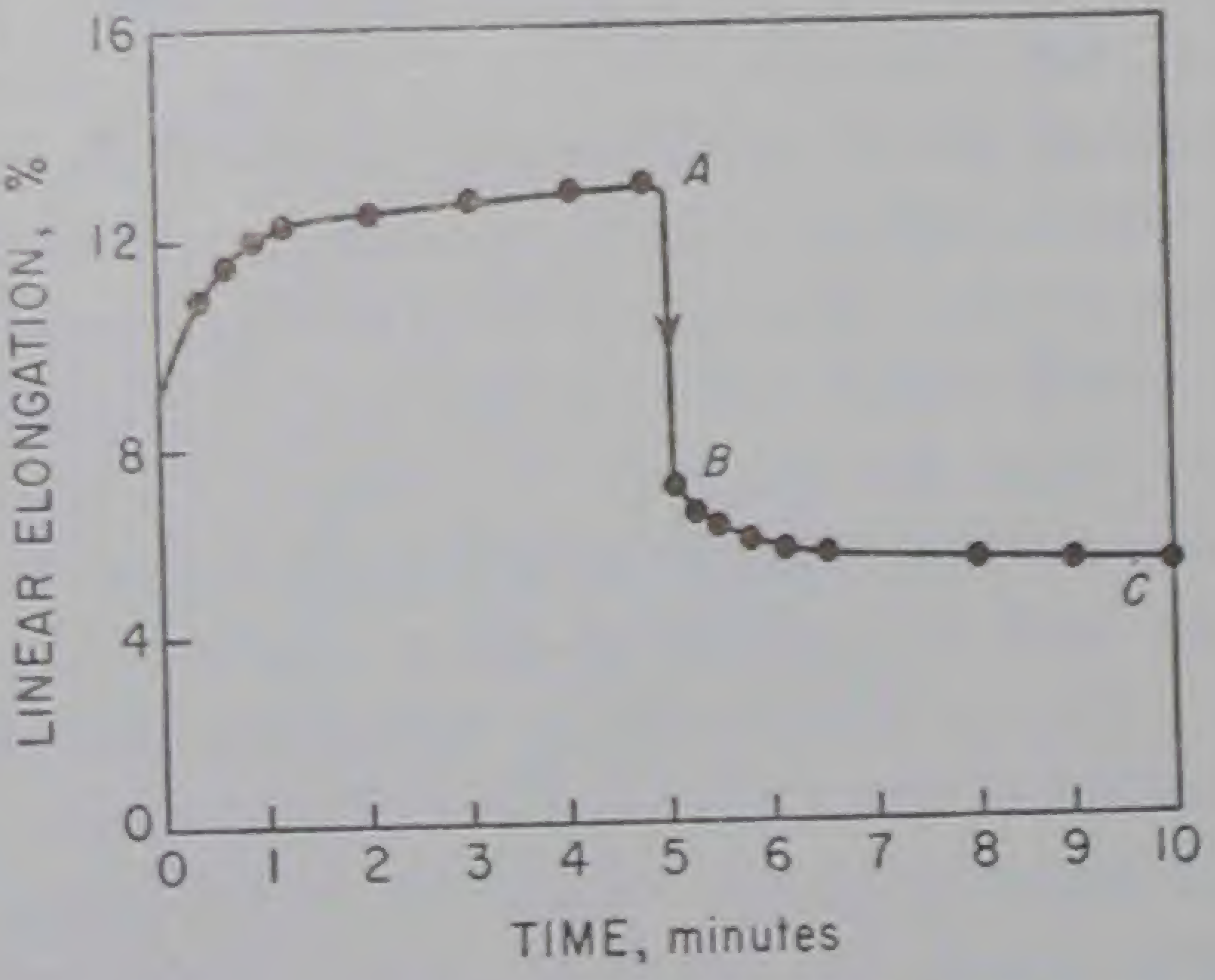

Fig. XVI-6. Strain recovery from a five-minute application of stress (2.75 kg./cm.). *A–B* is instantaheons recovery and *B–C* is creep recovery.

paper, particular emphasis being placed on one or the other, depending upon the use to which the paper is to be put.

If successively increasing weights are applied to a strip of paper and the stretching (straining) measured, a curve is obtained which starts out as a straight line (following Hooke's law), but which later curves toward the strain axis. In other words, the paper starts out as a purely elastic body and then, after a 1 to 2% strain, begins to exhibit flow. If the load is held constant, the paper will flow indefinitely until it breaks. This delayed flow, which is known as primary creep, occurs when printing papers are hung under their own weight for long periods in the print shop,[27] in wallpapers which stretch to conform to slowly sagging walls, and in other papers subjected to load over a period of time. Typical creep is shown in Figure XVI-5.[28] If the load is removed, the paper tends to recover its former shape partially, but part of the strain is non-recoverable, resulting in some permanent set.[28] The non-recoverable part of the flow which occurs in the first straining is sometimes referred to as secondary creep. Strain recovery is characterized by two separate parts, an instantaneous part and a time-dependent part, as shown in Figure XVI-6 for a paper made from 75% groundwood and 25% kraft.[29] A high rate of strain recovery is desirable in some kinds of printing papers to insure reproducible positioning of the paper under the various printing plates.[29]

If the strain on the paper is held constant, the stress will relax with time. Stress relaxation is the progressive reduction in stress which is required to maintain a constant elongation of the paper; it is somewhat similar to thixotropy in liquids. A paper with a high rate of stress relaxation will dissipate load more readily, and consequently will not break as readily as a paper with a low rate of stress relaxation. Bag papers require a high rate of relaxation in order to absorb the stresses to which the bags are subjected during use.[30] Bag papers with a high rate of relaxation and low tensile strength perform better than bag papers with a high tensile strength but low relaxation rate. Papers to be printed on a web press should have a high rate of stress relaxation to resist sudden stresses on the press. Newsprint made today has lower tensile strength than newsprint made years ago, but present-day newsprint works better because of its better flow properties.[31] Creped papers are widely used because of their high rate of relaxation. The tensile strength is lower than that of uncreped paper, but the creping process makes the paper more pliable and consequently more able to absorb sudden shocks without piling up stresses in the paper. In general, the relaxation of stress with time is rather rapid in the beginning (up to about 5 minutes), and later becomes much slower.

As pointed out above, rate of straining is very important, since paper which is rapidly strained tends to snap back to its original shape (exhibiting true elasticity), whereas paper which is slowly strained tends to hold

[27] J. Strachan, *Paper-Maker 114*, No. 2: 9–10 (Aug., 1947)

[28] B. Steenberg, *Svensk Papperstidn. 50*, No. 6: 127–140 (1947)

[29] S. G. Mason, *Paper-Maker*, 53–56 (June, 1948); *Pulp Paper Mag. Canada 49*, No. 3: 207–214, Convention Issue (1948)

[30] B. Steenberg, *Svensk Papperstidn. 50*, No. 15: 346–350 (1947)

[31] B. Steenberg, *Pulp Paper Mag. Canada 50*, No. 3: 207–214, 220, Convention Issue (1949)

its final shape (exhibiting flow). Creped paper tends to recover its crepe when stretched rapidly and released, but tends to lose its crepe when stretched slowly. When strained at very high rates, paper breaks into several pieces similar to the shattering obtained when materials like pitch or glass are strained rapidly. Rapid rate of straining increases the breaking strength of the paper.

Stress-strain measurements cannot be made with ordinary paper-testing instruments. The conventional pendulum type tensile tester is not suitable for measuring stress-strain relationship because of its low degree of accuracy, its complexity (neither stress nor strain is applied at a constant rate), and finally because the specimen is ruptured during the test. Steenberg[31] has described suitable apparatuses for measuring stress-strain. Two types of apparatus are used, one for slow rate of loading and one for very rapid rates of loading. In the slow instrument, the paper is strained between clamps and the stress in the sample recorded in the form of a stress-strain-time diagram by means of a beam scale which is kept in balance through a photocell and reversible motor connection. In the rapid instrument, the paper strip is strained by the action of a free-falling weight. Automatic stress-strain diagrams can be obtained under constant rate of loading or under constant rate of extension (straining). Typical stress-strain curves for relatively stiff, brittle paper (tested at 20% R.H.) and relatively plastic paper (tested at 98% R.H.) are shown in Figure XVI-7 based upon measurements made with the slow instrument.[31]

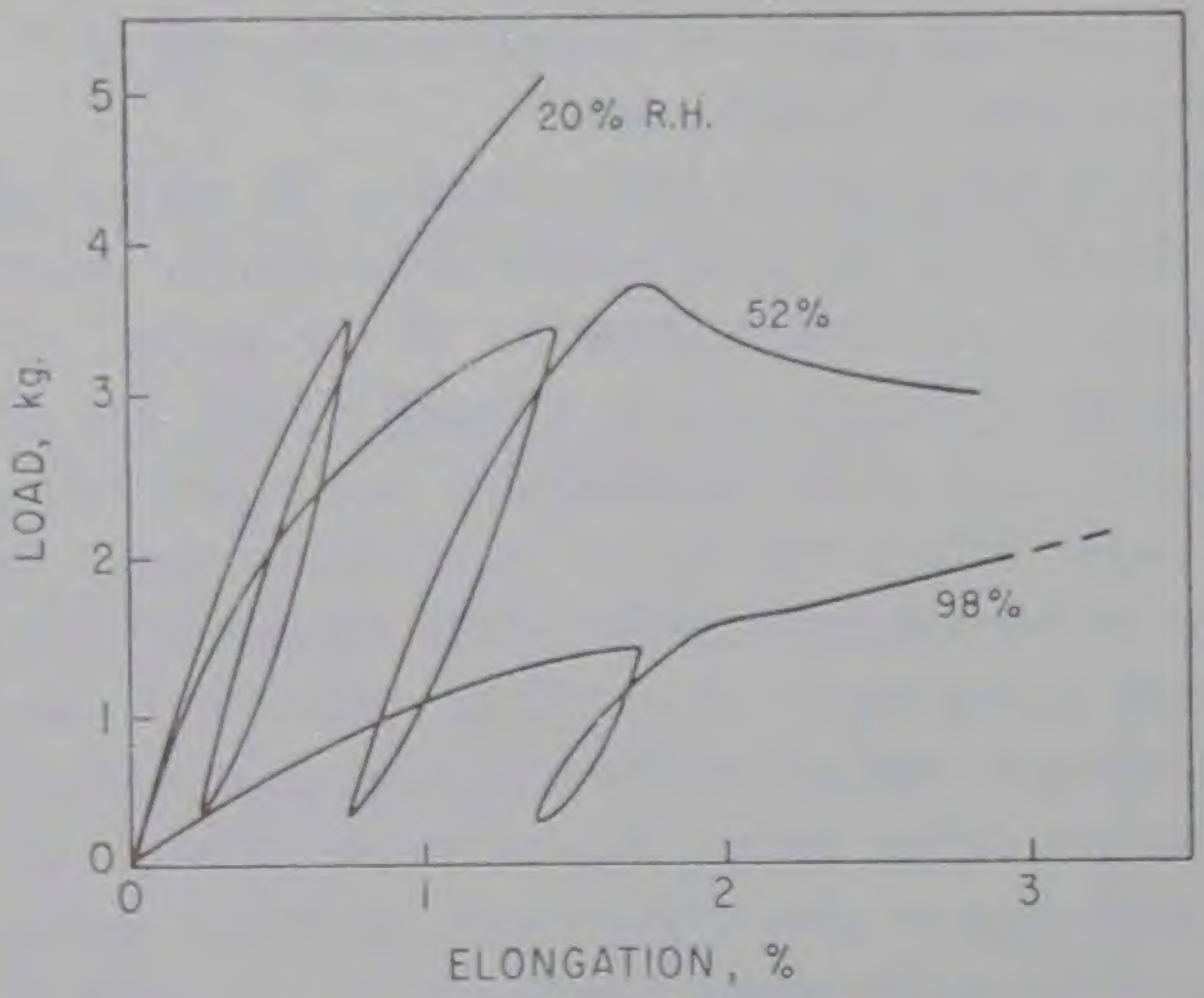

Fig. XVI-7. Stress-strain curves of paper made at different humidities.

Stress-strain measurements have the advantage of emphasizing the prerupture characteristics of paper, whereas most conventional tests measure the strength at rupture. From a practical standpoint, prerupture behavior of paper is a more important consideration than the strength at rupture, since paper is ordinarily not used to the point of rupture. The area under the stress-strain curve gives the energy per unit of volume. When multiplied by the cross-sectional area and length of the sample, the total energy which the material can absorb is obtained. At very high rates of straining (impact), Steenberg[32] points out that the inertia as well as the rheological properties influence the response. Under these circumstances, stresses and strains are propagated as shock waves so that stress is unevenly distributed in the sample. This may result in breaking of the paper in more than one spot, not always at the weakest point. As the velocity is increased, a point called the critical velocity is reached. At this point, the inertia becomes equal to the cohesive forces and failure occurs immediately at the impact point, the stress at any adjacent point being zero. The critical velocity for newsprint appears to be about 23 m. per second.[32]

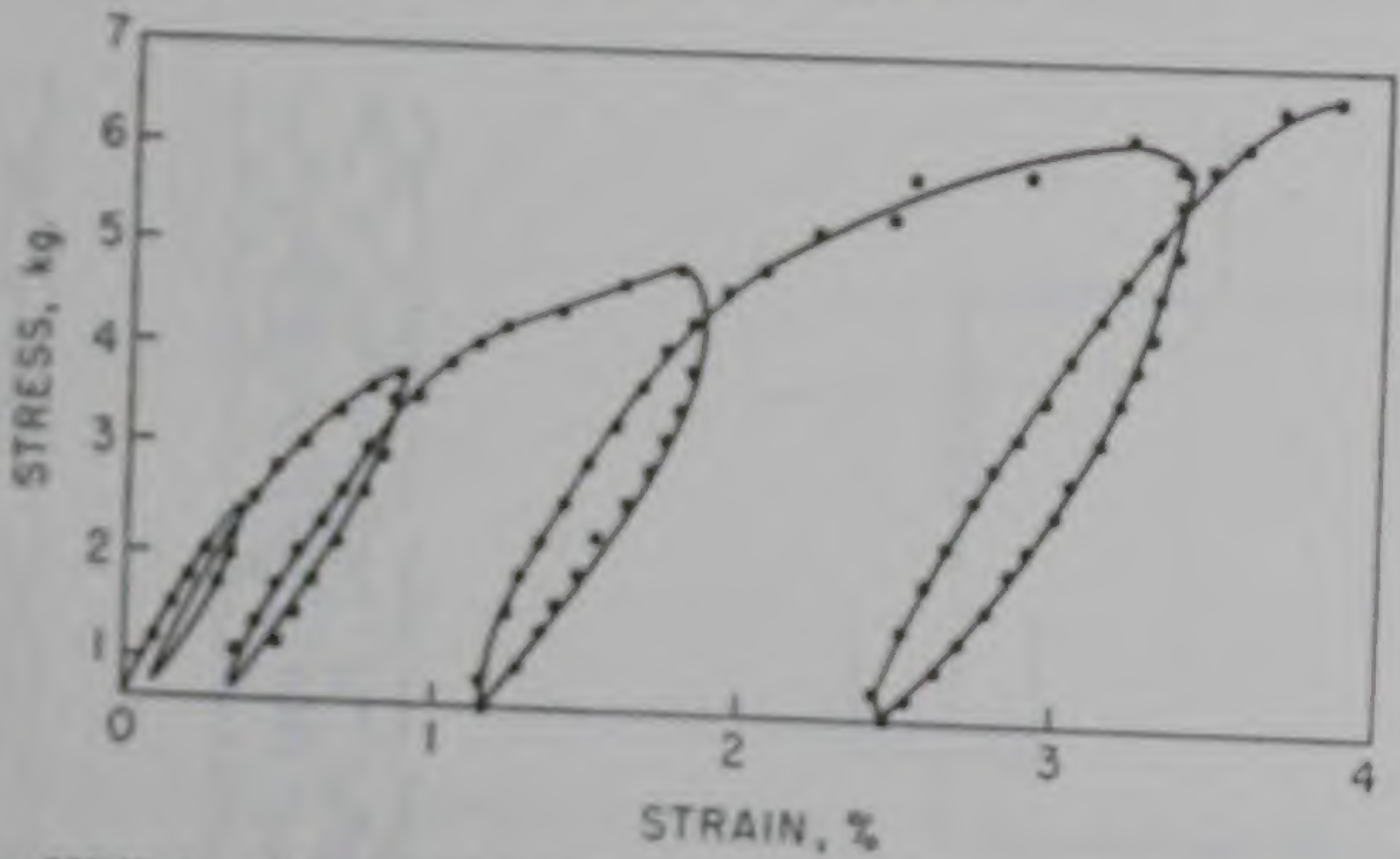

Fig. XVI-8. Effect of loading and deloading on bleached sulfate paper (45° against the machine direction).

Successive loading and deloading of paper increases the length of the unloaded paper, as shown in Figure XVI-8, so that the same curve is not obtained on ascending and descending stress.[35] In obtaining the data in this figure, the paper was stretched at a constant rate of about 0.003 mm. per second and the force measured at each point. At a given point, the motor used for stretching was reversed and the paper allowed to recover its length at the same rate at which it was originally stretched. This gives a downward curve which is slightly concave. When the paper is strained in a second cycle, the upcurve is slightly convex for a while and then decreases abruptly when the maximum stress obtained in the first cycle is reached. Apparently the first straining cycle results in a change in the flow properties of the paper removing the secondary creep and leading to a pronounced yield point at the maximum stress of the first cycle. This phenomenon is known as memory effect, since the curve tends to continue in the same path started in the first cycle. Thus, from an examination of the stress-strain curve, it is possible to determine the previous strain to which the paper had been subjected, since the stress-strain curve levels off at this point.

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[32] O. Andersson and B. Steenberg, *Svensk Papperstidn.* 53, No. 1: 1–7 (Jan. 15, 1950)

A stress relaxation curve can be obtained at the same time that the stress-strain diagram is obtained by stopping the moving clamp and plotting load versus time at constant length. As noted previously, there is a rapid loss in stress at first, followed by the very much slower loss (see Fig. XVI-6). The loss in stress is generally small compared with the over-all stress on the sample.

The stress-strain relationships exhibited by paper can be understood by analogy with a mechanical model consisting of a spring and a dashpot connected in series (Maxwell element) and a spring in parallel, as shown in Figure XVI-9. When forces are applied to the model, both springs are stretched in the early stages, but the dashpot is not appreciably moved. This is the period of elastic flow when the stress-strain curve is a straight line. When greater force is applied, the dashpot is moved and the stress-strain curve tends to bend toward the strain. Steenberg's concept of a strained and unstrained paper is shown in Figure XVI-10.[33]

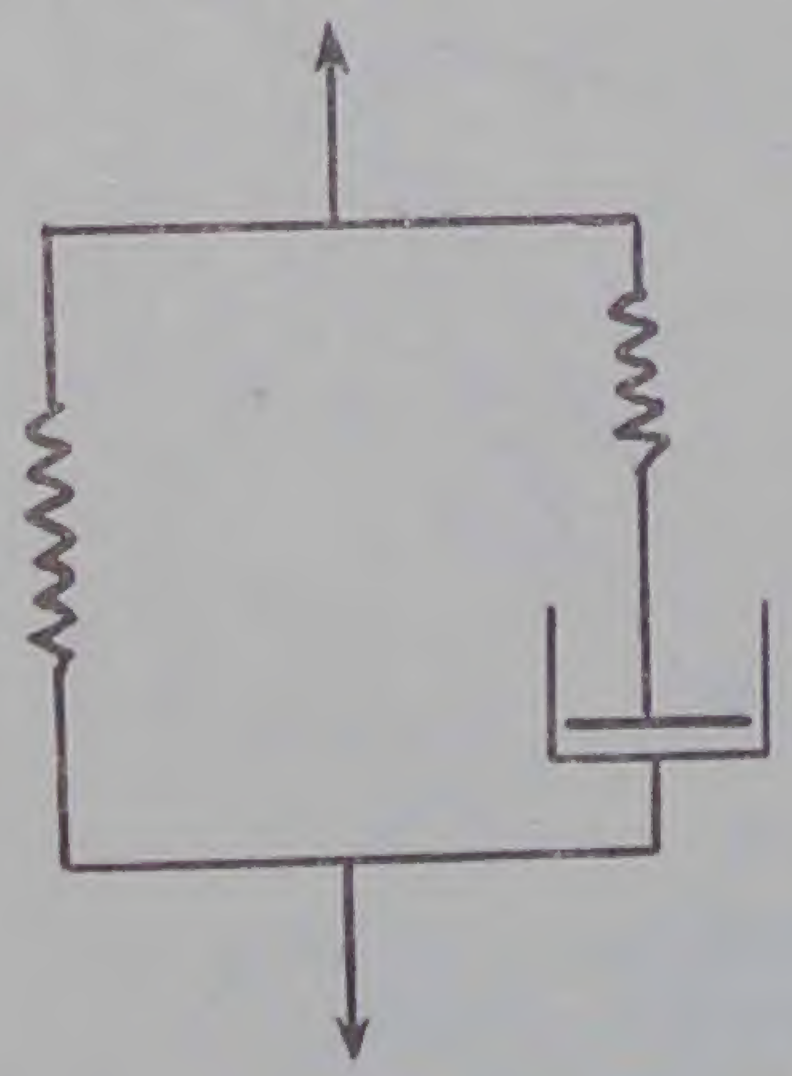

Fig. XVI-9. Mechanical model to illustrate stress–strain relationships of paper.

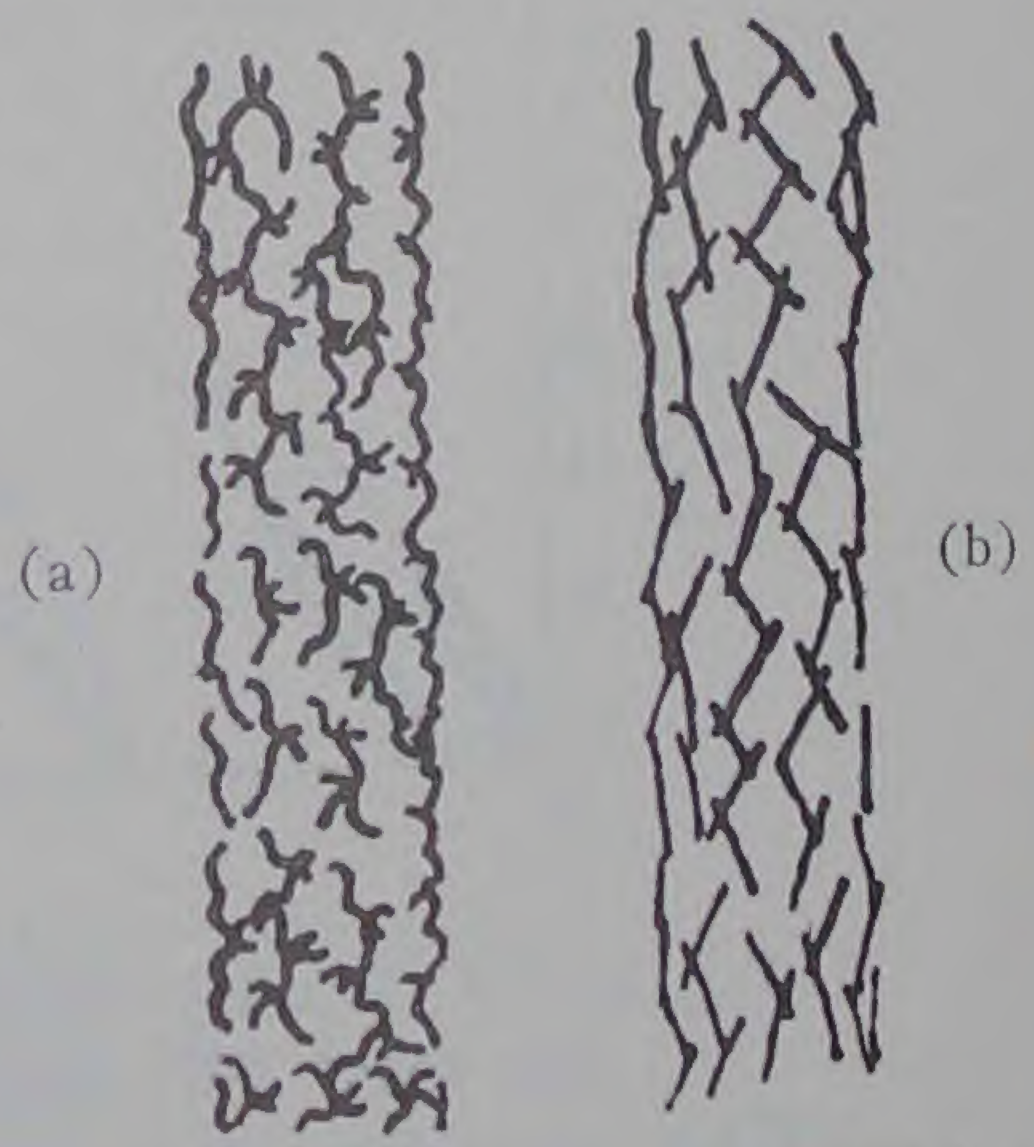

Fig. XVI-10. Diagrammatic sketch of unstrained (a) and strained (b) paper.

Moisture content greatly changes the stress-strength relationships of paper, affecting the elastic, as well as the plastic properties of the paper.[34] Increased moisture content increases the flow properties or, in other words, elongates the stress-strain curve so that the load is less, but the per cent elongation is much greater, as previously shown in Figure XVI-7, where stress-strain curves are plotted for papers conditioned at three different relative humidities. Paper bags are sometimes filled under conditions of high relative humidity, because the paper has a greater rate of relaxation when slightly moist. This increased relaxation permits the bags to be filled with less breakage, even though the tensile strength of the paper is lower at the high humidity.

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[33] B. Steenberg, *Pulp Paper Mag. Canada 50,* No. 3: 207–214, 220, Convention Issue (1949)

[34] O. Andersson, B. Ivarsson, A. H. Nisson and B. Steenberg, *World's Paper Trade Rev. 133,* No. 1: 2–8TS (Jan. 5, 1950)

Ordinarily, tensile strength and stretch measurements are made in only two directions, the machine and the cross directions. It is desirable in the case of some papers to know something about the strength of the paper in all directions. Typical stress-strain diagrams showing the variation in stress and corresponding elongation at different angles from the machine direction are shown in Figure XVI-11 taken from work by Steenberg.[35] Similar information is also illustrated in Figure XVI-12, showing breaking load versus extensibility for test strips cut in different directions of a Fourdrinier paper. It can be seen from these curves that the flow is small in the machine direction (90°), but is very large in the cross direction.

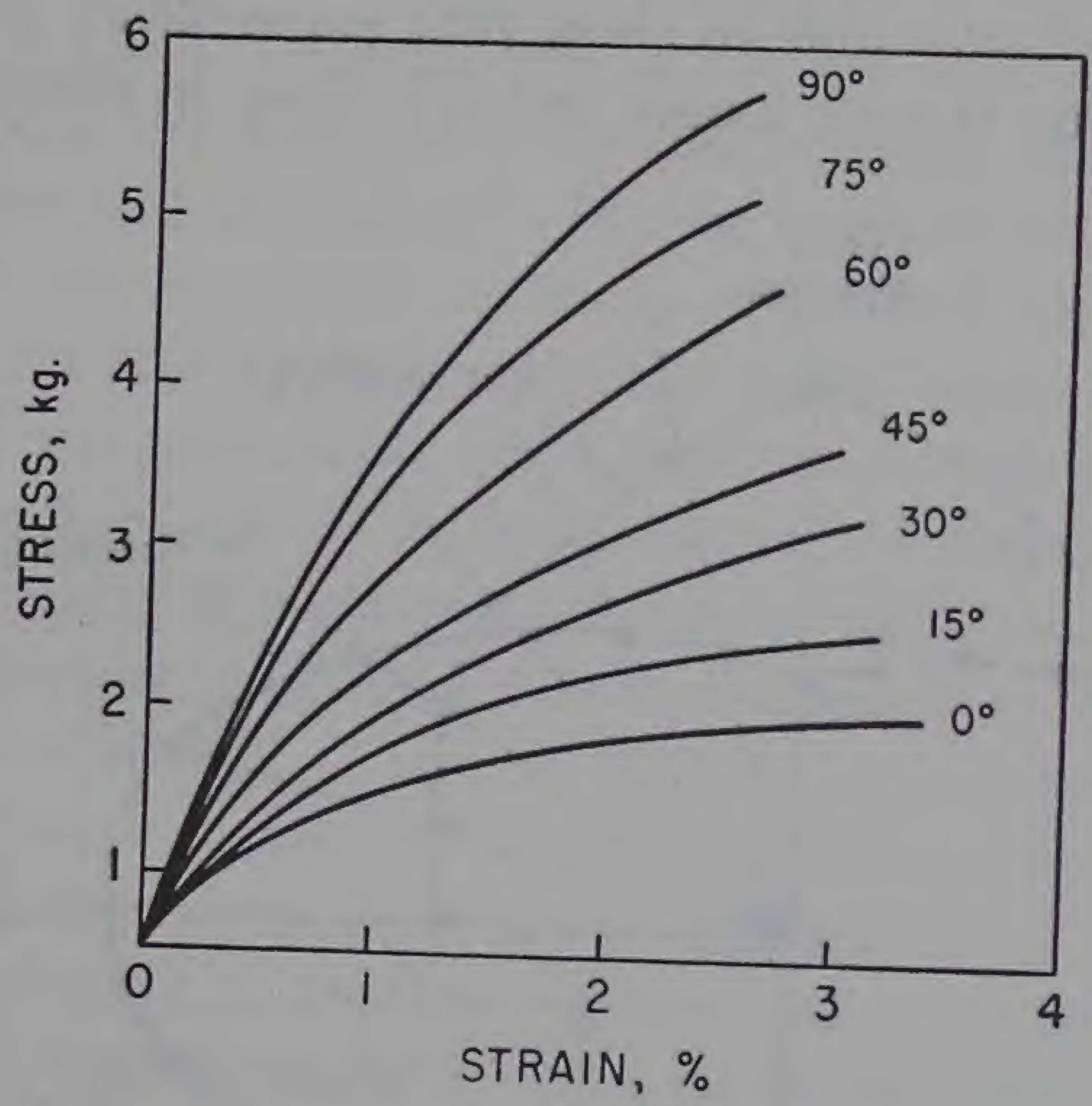

Fig. XVI-11. Stress–strain diagrams for test strips cut in different directions of the paper (machine direction = 90°).

Steenberg and coworkers[35–39] have made extensive stress-strain studies to determine the effects of paper machine operation, history of the paper, and other similar variables on the stress-strain properties. Their work indicates that a measurable part of the strength variations between the machine and cross directions results from the draw on the paper machine. A marked difference was obtained in flow in the cross direction across the width of the sheet, paper taken from the edges showing far more capacity for irreversible flow than paper taken from the middle of the sheet. On the other hand, there is little variation in the machine direction flow across the width of the sheet due to the tension on the paper in this direction during drying. Steenberg[39] was able to show that paper dried experimentally under minimum tension is very tough, but is lacking in stiffness. Paper dried under increasing tension becomes stiffer and stiffer, until an almost perfectly elastic body is obtained at maximum tension. The ultimate tensile strength was not increased to any appreciable extent in these experiments of drying under tension, although other investigators have reported that draw increases tensile strength[40] (see Ch. VIII). Rance[41] has shown that the expansivity of paper on wetting is reduced by an amount proportional to the degree of permanent set obtained on prestraining. Thus, the tension exerted on the sheet during drying on the paper machine is a factor in reducing the expansivity of the paper in the machine direction. Wet pressing affects flow properties, as does calendering, which tends to break down the paper structure and almost entirely eliminate secondary creep. The viscosity of paper calculated from the stress-strain curve tends to increase

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[35] B. Steenberg, *Svensk Papperstidn. 50,* No. 6: 127–140 (Mar. 31, 1947)

[36] B. Steenberg, *Svensk Papperstidn. 50,* No. 15: 346–350 (Aug. 15, 1947)

[37] B. Ivarsson and B. Steenberg, *Svensk Papperstidn. 50,* No. 18: 419–432 (Sept. 30, 1947)

[38] B. Ivarsson and B. Steenberg, *Svensk Papperstidn. 51,* No. 2: 23–30 (Jan. 31, 1948)

[39] B. Steenberg, *Pulp Paper Mag. Canada 50,* No. 3: 207–214, 220, Convention Issue (1949)

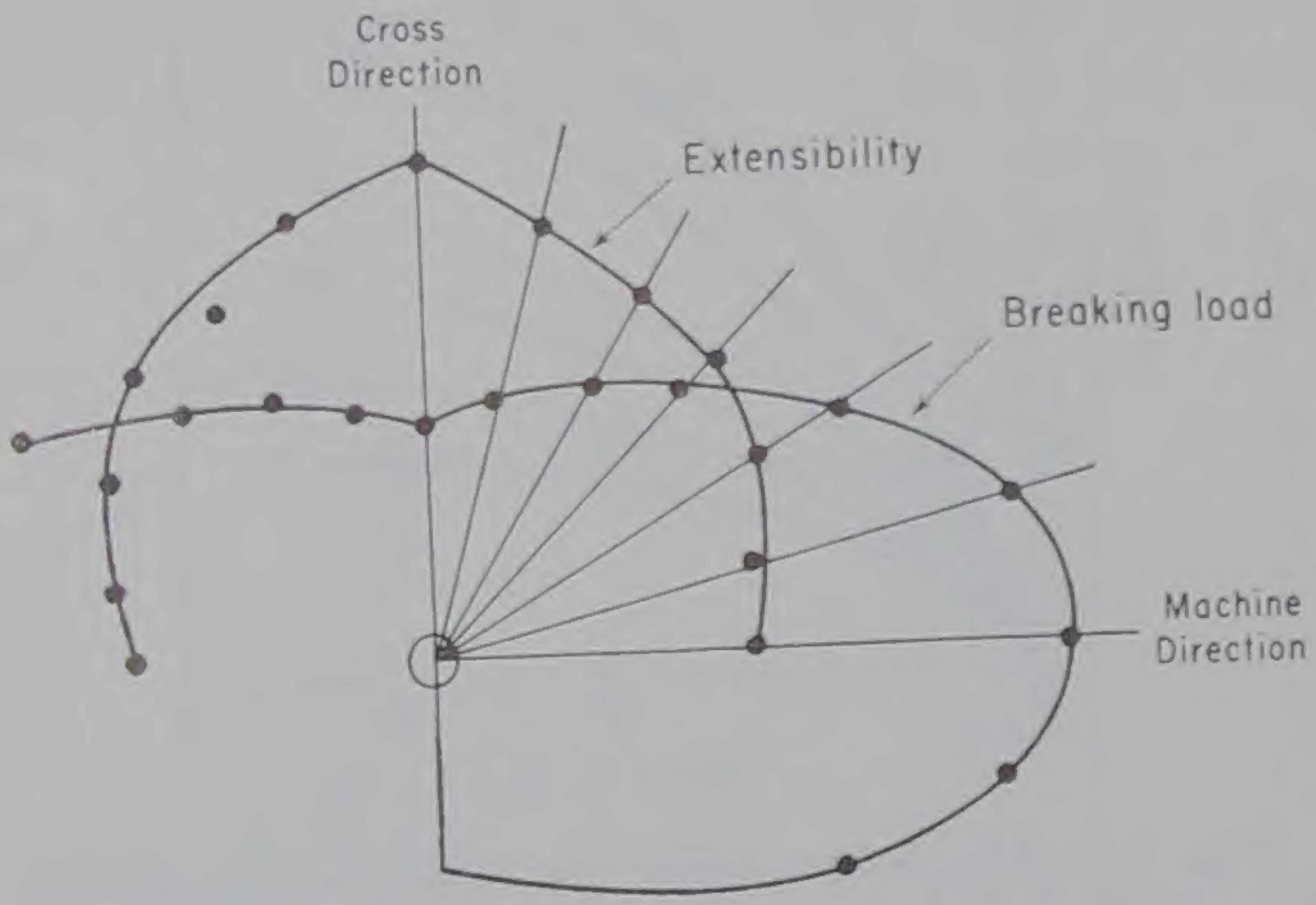

Fig. XVI-12. Breaking load versus extensibility in different directions of a Fourdrinier paper (arbitrary units).

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[40] J. E. Sapp and W. F. Gillespie, *Paper Trade J. 124,* No. 9: 120–123 (Feb. 27, 1947)

[41] H. F. Rance, *Paper-Maker* 22–32, 49, 50, 51, Midsummer Issue (1949)

rapidly with beating in the early stages until a maximum is reached, and then to decrease slightly for prolonged beating.[42]

Stiffness

The similarity between paper and other structural materials has already been mentioned. This similarity should make it possible to determine the rigidity of paper by methods used with metals, wood, and other structural materials. Stiffness is related to the flow properties because it depends upon the ability of the layer on the outside curve of the material to stretch and on the ability of the inside layer of the curve to undergo compression.

In the case of heavy paperboards which are stiff enough to act as a beam, static bending has been used for determining stiffness, modulus of rupture, and modulus of elasticity.[43] In one method of testing paperboard by static bending, the specimen is freely supported horizontally at both ends on rollers and a load applied uniformly at the center of the span. The application of load sets up a stress and a proportional resistance to deformation (strain). Load is applied at constant rate at the center of the beam usually by adding water at a constant rate to a pail attached to the strip of paper through a stirrup. The deflection is measured by means of a vertical scale or a deflection needle. Load in pounds or ounces (stress) can be plotted against deflection in inches (strain) to give a straight line up to the elastic limit, after which strain increases at a greater rate than stress. Brittleness can be determined by multiplying the load at the elastic limit by 100 and dividing by the load at rupture. In a perfectly brittle body, this value will be 100 per cent since a perfectly brittle body will break at the first deflection.

Flexural rigidity is proportional to Young's modulus, which is the ratio of the unit stress to the unit strain below the elastic limit, times the moment of inertia. Papermaker's stiffness, on the other hand, is a measure of the ability of the paper to support its own weight and is proportional to Young's modulus (E) times the moment of inertia (I) divided by the basis weight (W), i.e., EI/W. Stiffness can be determined by the following formula:[44, 45]

$$\text{stiffness} = \frac{ET^3}{12} \times \frac{W}{L^2}$$

where E (Young's modulus) equals the stress/strain in the direction of axis of the test strip, T is thickness of sample, L is length of sample, and W is width of sample. Young's modulus, sometimes called the modulus of elasticity, is a fundamental property which is independent of dimensions. It is expressed in dynes per square centimeter, or in pounds per square inch, and is defined as follows:

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[42] O. Andersson, B. Ivarsson, A. H. Nisson and B. Steenberg, *World's Paper Trade Rev. 133*, No. 1: 2–8TS (Jan. 5, 1950)

[43] C. C. Heritage, E. R. Schafer and L. A. Carpenter, *Paper Trade J. 89*, No. 17: 182–185 (Oct. 24, 1929)

[44] *Idem.*

[45] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 104*, No. 21: 287–290 (May 27, 1937)

$$\text{Young's modulus} = \frac{\text{tensile stress}}{\text{tensile strain}} = \frac{\text{force/area}}{\dfrac{\text{change of length}}{\text{original length}}}$$

$$= \frac{\text{force} \times \text{original length}}{\text{area} \times \text{change of length}}$$

The higher Young's modulus, the higher the stiffness, and since Young's modulus is numerically equal to stress/strain per unit area, increased stiffness is obtained by reducing the strain for a given load.

There are several instruments for testing the stiffness of paper, but these fall short of a true stiffness measurement because they displace the paper beyond its elastic instrument, and because they express the results in arbitrary values. Instruments for measuring papermaking stiffness are usually based upon one of the following principles: (*1*) a measurement of the force required to bend a strip of the paper through a given angle; (*2*) a measurement of the angle through which a strip of paper is bent when subjected to a definite force; (3) a measurement of the angle through which a strip of paper bends under its own weight when held in a horizontal fixed position.

In the Taber instrument, a specimen (1½ × 2¾ in.) is fastened in a clamp on a pendulum. Load is applied to the lower end of the specimen by rollers attached to a power-driven disk so that the resulting torque deviates the pendulum from the vertical. The end point is indicated by the alignment of the pendulum with the 15° mark on the loading disk. In carrying out the test, the force should be applied slowly and the average of the deflection taken for both directions.

The Gurley instrument measures the bending moment which the paper can withstand in both directions by deflecting a small weighted pendulum. The sample is cut to overlap the top of the pendulum by ¼ in. so that the sample must be bent sufficiently to shorten it by this distance. The size of the sample and the weight on the pendulum can be varied, depending upon the stiffness. All combinations can be reduced to a common basis of a sample 1 in. in width and 3½ in. in length by use of suitable factors. Motor-driven and hand-operated models are used. Stiffness readings on the Gurley and Smith-Taber instruments measure essentially the same property.[46]

Stiffness can be measured in the Clark tester as the critical length of a

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[46] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 104*, No. 21: 287–290 (May 27, 1937)

2-in. strip of paper which just falls over when the framework of the instrument is rotated through 90°.[47, 48] Stiffness is then calculated as $L^3/100$, where L is the average effective overhang in inches.

The Tinius Olsen stiffness tester is well designed to measure stiffness of heavy paper. The specimen is clamped at one end and bent by applying a load at the free end. There are two scales, a load scale and an angular deflection scale. Actual pounds load is obtained from the load scale reading times the bending moment used (inches–pounds on weight) divided by the bending span in inches. Stress-strain curves can be plotted as load scale reading versus angular deflection. Apparent modulus of elasticity can be calculated from the data using the following formula:

$$E = \frac{4S}{wd^3} \times \frac{M \times \text{scale reading}}{100\phi}$$

where E = apparent modulus of elasticity
S = span in inches
w = width in inches
d = thickness in inches
M = moment weight on pendulum
ϕ = angular deflection in radians in straight section of the curve.

The flexural resistance of heavy boards can be measured in a regular tensile tester, using a special device which permits the application of load at the center of a strip of the board held at both ends. The results can be reported in load at failure, or maximum load, if there is no failure. The deflection in inches in both directions can also be determined.

The rigidity of heavy papers is sometimes measured in a compression resistance test known as the ring crush test. In this test, a specimen of paper (usually 0.5 × 2.0 in.) is inserted in a specimen holder in the form of a ring. The ring of paper is then compressed between two platens and the maximum applied load is measured at failure. This test is used mostly for measuring the edgewise rigidity and crush resistance of corrugating medium used for making corrugated board.

Stiffness is greatly affected by the thickness of the paper, theoretically as the cube of the thickness. Smith[49] found, in the case of cylinder machine boards, that the rigidity increased as the cube of the thickness when density is kept constant, and as the square of the thickness when weight is kept constant. He found rigidity to be proportional to the first power of the density at a given thickness. According to Smith's data, the ratio of rigidity in the machine direction to that in the cross direction of cylinder machine boards

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[47] TAPPI Tentative Standard T451-m-45

[48] J. d'A. Clark, *Paper Trade J. 100*, No. 13: 169–172 (Mar. 28, 1935)

[49] S. F. Smith, *World's Paper Trade Rev. 99*, No. 6: 403–404, 406, 408, 442, 444, 446; No. 7: 483, 486, 520, 522, 525, 526 (Feb. 10, 17, 1933)

is from 3.2 to 1 to 4.3 to 1, and this ratio is maintained independently of the speed of the machine, thickness of the board, or of the type of fiber.

Papermaking stiffness is related to brittleness, rattle, and other less definable paper qualities. Papers made from highly beaten stocks (bond and glassine) have higher stiffness than papers made from lightly beaten stocks (toweling and filter papers). Papers made from pulps high in hemicellulose content (e.g., straw pulps) are stiffer than papers made from pulps low in hemicellulose content (e.g., alpha pulps). Papers made from short-fibered pulps (straw, chestnut, and groundwood) are generally stiffer than papers made from longer fibered pulps. Papers made from chemical wood pulp generally have a higher stiffness to tear ratio than do rag papers.[50] Van den Akker[51] conjectures that stiffness in thin papers is more a matter of individual fiber rigidity whereas stiffness in thick papers is more a matter of extent of fiber bonding. The addition of starch or sodium silicate to the furnish increases stiffness. Increasing the moisture content of the paper appreciably lowers the stiffness.[52]

Stiffness is very important in boxboards, since the utility of a box depends upon its ability to resist bending when filled. The important fundamental property in this case is the elastic rigidity, since a satisfactory boxboard is probably not bent beyond its elastic limit. Stiffness is of very great importance in index bristols, card middles, typing papers, and playing cards, where the paper must stand upright during use. A certain amount of stiffness is desirable in bond paper where it is a factor in the handle of the paper.[53] These papers are customarily made by heavy beating and by the addition of starch or sodium silicate to the furnish. Stiffness is very important in corrugating medium for corrugated board, and hence pulps are chosen which will give high stiffness (e.g., chestnut, straw, or semichemical). On the other hand, stiffness is undesirable in such papers as tissues, toweling, printing papers, and labels. Plasticizers are added to glassine to lower the stiffness. Paper label stock is sometimes pebbled to reduce the stiffness.

Tensile Strength

Tensile strength is a measure of the resistance of paper to direct tension. It is defined as the force required to break a strip of paper which has a specified length and a width of 15 mm. Most tensile testers use a pendulum for applying load, which is free to rotate in a vertical plane. The paper is clamped between two jaws (both of which move during the period of applying load), and then the pendulum is swung out from its vertical resting position by a hand crank or by a motor. This applies an increasing load to the paper until finally the strip breaks. The load at which the strip breaks is termed the tensile strength and is reported in kilograms for 15 mm. of width, or in pounds per inch of width. Conversion from one to the other can be made on the basis that 1 kg./15 mm. is as 3.73 lb./in. of width.

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[50] C. A. Minor and J. E. Minor, *Paper Ind.* (Apr., 1935). (Obtained from reprint.)

[51] J. A. Van den Akker, *Tappi 33*, No. 8: 398–402 (Aug., 1950)

[52] F. W. Adams and J. Bellows, *Paper Trade J. 96*, No. 9: 117–120 (Mar. 2, 1933)

[53] J. Strachan, *Paper-Maker 113*, No. 2: 9–11 (Feb., 1947)

Tensile strength more nearly approaches a fundamental measurement than other conventional strength measurements made on paper. Tensile strength is a component of the more complex bursting, folding, and tearing strengths which are discussed in the following sections. However, tensile strength as measured in the paper industry is not a true tensile strength, since it measures the breaking load per unit of width rather than per unit of area. It would be more appropriate to use the term "breaking strength" in reference to this test, but since the term "tensile strength" has become well established, it is customarily used throughout the industry.

For ordinary purposes, tensile strength as measured in the paper industry is indicative enough of the utility of the paper, since paper is ordinarily used in sheet form, but for some purposes, such as when paper is used as a structural material, "true" tensile strength would be a more useful term. A useful figure expressing a tensile strength-weight ratio can be obtained by dividing the tensile strength of the paper by the weight of the paper. Another useful figure is the breaking length, a strength-to-weight ratio which indicates the length of a strip of paper required to cause the strip to break under its own weight. Breaking length in meters can be determined by the following relationship:

$$\begin{matrix}\text{breaking length}\\ \text{(meters)}\end{matrix} = \begin{matrix}\text{tensile strength}\\ \text{(kilograms)}\end{matrix} \times \frac{\text{length of strip (meters)}}{\text{weight of strip (kilograms)}}$$

Breaking length is a function of tensile strength, thickness, and basis weight.

In making tensile strength determinations, the time during which the load is applied is an important factor. As previously shown, paper will break under reduced load if the time of application of the load is increased. Conversely, the apparent tensile strength will be increased if the paper is broken rapidly.[54] This is due to the flow in the paper and to the time element involved in the separation of fibers just prior to rupture. Motor-driven tensile testers are preferred over hand-driven models because of their more uniform rate of loading.

The length of the paper strip influences the tensile strength. The standard strip length is 180 ± 10 mm., but different lengths can be used, depending upon the size of the available sample. The length of the sample should be specified, inasmuch as short strips give higher readings than long strips, because of a greater chance for imperfections in long strips. There may be as much as 10% difference in results between a strip 100 mm. and a strip 180 mm. in length taken from the same paper. In testing handsheets, it is customary to use a strip 100 mm. in length because of the small size of the sample. Specimens smaller than 50 mm., the shortest length which can be used in the ordinary machine, may be tested by extending the strip with strips of strong gummed kraft paper.

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[54] R. C. Griffin and R. W. McKinley, *Paper Trade J.* *102*, No. 2: 20–21 (Jan. 9. 1936)

Tensile strength is always greater in the machine direction than in the cross direction because of the greater alignment of fibers in the machine direction. Increasing the weight of the paper, of course, increases the tensile strength. However, Doughty[55] has shown that the ultimate tensile strength in pounds per square inch decreases with increasing basis weight (when the solid fraction remains the same). This can be attributed principally to variation in fiber orientation.

It is interesting to calculate what the theoretical upper limit of tensile strength would be if the paper were held together by the same force as the individual fibers. The standard width of the paper strip used in the tensile test is 15 mm., or 15,000 microns, and assuming that the thickness of a strip of paper (bond) is 0.004 in. or 101.6 microns, the calculated area of the strip would be 1,524,000 square microns. Assuming that the paper is composed of 65% fiber (the rest being air), the area of the fibrous part of the strip should be equal to $1{,}524{,}000 \times 0.65$, or 990,600 square microns. Clark[56] gives the area of a spruce fiber as 160 square microns, which means that there should be room for 6,191 fibers in the cross-sectional area of the test strip. Then, using Ruhlemann's[57] value of 10 g. for the tensile strength of individual spruce fibers, the tensile strength of the strip should be $10 \times 6{,}191 = 61{,}910$ g., approximately 62 kg., if the strip were composed of continuous inter-fiber bonds. However, the actual tensile strength of bond paper 0.004 in. in thickness is approximately 10 kg. which is only about 16% of the theoretical 62 kg., thereby attesting to the relative weakness of the bonds between the fibers, compared to the much stronger bonds within the individual fibers. In the same connection, Stamm[58] reports that paper has a tensile strength of only 0.5 to 8.0 kg. per square millimeter compared to a value of 80 kg. for a well-oriented viscose film.

It is obvious from the above calculations that the amount and quality of fiber bonding is the most important factor affecting tensile strength. The brittleness of the bond is of relatively little importance. Parsons[59] has shown that there is a linear relation between the tensile strength of paper and the area of fibers in optical contact in the early stages of beating. The relation is the same, regardless of whether the area of fiber contact is varied by increased beating or by increased wet pressing, thus indicating the fundamental importance of fiber bonding. Tensile strength tends to show a slight drop if the pulp is excessively beaten (due to destruction of fiber structure), but there is no decrease in tensile strength when the sheet is increased in density by wet pressing (see Figure XVI-3). Fiber length is believed to play a role in tensile strength of paper. Kane[60] believes that moderate variations in fiber length have little effect on tensile strength, but Clark[61] reports that tensile strength is proportional to the square root of the average fiber length by weight.

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[55] R. H. Doughty, *Paper Trade J. 93*, No. 15: 162–167, 172 (Oct. 8, 1931)

[56] J. d'A. Clark, *Paper Trade J. 118*, No. 1: 1–6 (Jan. 6, 1944)

[57] E. Ruhlemann, Thesis, Tech. Hochschule, Dresden (1925) through J. d'A. Clark, *Paper Trade J. 118*, No. 1: 1–6 (Jan. 6, 1944)

[58] A. J. Stamm, "Colloid Chemistry of Cellulose Materials," *U. S. Dept. of Agri., Misc. Publ. 240*, (1936)

[59] S. R. Parsons, *Paper Trade J. 115*, No. 25: 314–322 (Dec. 17, 1942)

Tensile strength is important in newsprint and other papers printed on a web press where high tensile strength helps to resist the tension on the press. Tensile strength is an important property of bag and wrapping papers. High tensile strength is needed in asphalt-saturated papers to resist the stresses set up when the saturated paper is festooned during drying. It is particularly important on gummed paper, spin paper, binder twine, and cable wrapping paper. These papers are usually made from raw, unbleached pulps and are formed on the paper machine to obtain as much machine direction tensile strength as possible. Government specifications for kraft bag paper (UU-S-48a, Sept., 1945) permit compensating for below-standard tensile strength by a compensating increase in tearing strength in the ratio of five units of M. D. tearing strength to one unit of C. D. tensile strength.

One special type of tensile strength measurement is the zero-span test by which the tensile strength is measured in a special device in which the two jaws of the tensile tester are set up against each other with zero span.[62] The principle behind this test is that the individual fibers in the paper span the gap between the jaws, and hence the test indirectly indicates the intrinsic strength of the individual fibers. Jacobsen[63] obtained the following values for the zero-span tensile test on different pulps:

Pulp	Breaking length
Unbleached kraft	14,000 meters
Unbleached sulfite	7,700 meters
Unbleached soda	4,600 meters

The zero-span tensile test is not a fundamental test and is, at best, only an arbitrary indication of ultimate fiber strength. It is useful, however, for measuring the loss in individual fiber strength resulting from overbleaching, high acidity, or other degrading effects.

[60] M. W. Kane, *Tappi 32,* No. 12: 546–552 (Dec., 1949)

[61] J. d'A. Clark, *Paper Trade J. 110,* No. 9: 122–124 (Feb. 29, 1940)

[62] J. d'A. Clark, *Paper Trade J. 118,* No. 1: 1–6 (Jan. 6, 1944)

[63] P. M. Hoffman Jacobsen, *Paper Trade J. 81,* No. 22: 216–217 (Nov. 26, 1925)

The ratio between the normal tensile strength and the zero span tensile strength is, to some degree, an indication of the amount of interfiber bonding, since the zero-span test does not appreciably increase after a limited amount of fiber bonding. It is not appreciably affected by the addition of cementing agents,[62] and beyond a certain minimum amount, it is not greatly affected by further beating, as shown in Table VIII taken from work done by Clark[62] on the beating of west coast sulfite in a laboratory kollergang. Hence, by comparing the zero-span tensile strength with the normal tensile strength, it is possible to determine what part of the sheet strength is due to fiber strength and what part is due to fiber bonding. The zero-span tensile test is also useful for measuring the relative degree of orientation of fibers in the machine and cross directions of the paper.

TABLE VIII

EFFECT OF BEATING IN KOLLERGANG ON REGULAR TENSILE STRENGTH AND ZERO-SPAN TENSILE STRENGTH OF SPRUCE PULP

Sample	Regular tensile strength		Zero-span tensile strength	
	Tensile, kg.	Breaking length, meters	Tensile, kg.	Breaking length, meters
Unbeaten	3.6	1750	19.2	9,450
Beaten, 4 r.p.g.	7.8	3800	24.2	11,900
Beaten, 8 r.p.g.	10.5	5120	26.4	12,700
Beaten, 32 r.p.g.	12.6	6300	26.5	13,200
Beaten, 64 r.p.g.	13.9	7050	27.4	13,900

6–10 r.p.g. represents treatment given to normal bond paper. Zero-span breaking length is calculated as:

$$\frac{\text{kg. breaking load} \times 200{,}000}{\text{basis weight/sq.in.} \times 3}$$

On certain grades of paper it is desirable to measure the tensile strength after the paper has been soaked in water for a standard length of time. This measurement, which is known as the wet tensile strength, is discussed in Chapter XII.

Stretch

Stretch is the amount of distortion which paper undergoes under tensile stress. It is usually measured on the tensile tester at the same time that the tensile strength is measured.

In measuring stretch, an initial stress of about 0.5 lb. should be applied to the paper in order to remove any cockles or waviness. This can be done by applying tension with the fingers. After the strip is clamped, the stretch indicator is engaged with the lower clamp and load is then applied. The elongation at rupture is read from the stretch indicator to the nearest 0.5 mm. For strips exactly 100 mm. in length, the reading can be directly reported as per cent stretch. However, strips of 180 mm. in length are preferred for greater accuracy, and in this case, the percentage stretch must be calculated. Higher readings are obtained from shorter strips, but the results are not greatly affected by the rate of loading or by the width of the strip.

The stretch of creped papers can be measured in the above manner, but shorter strips are generally required in order to keep the reading on the scale. No tension should be applied prior to clamping in the case of creped papers. The rate of loading affects, to some extent, the results obtained on creped papers.

The stretch mechanism on the tensile strength tester is not very accurate because of deficiencies in the release mechanism. For precise work or for papers with stretch less than 2%, a special stretch tester should be used. One instrument[64] especially designed for measuring stretch consists of a device for clamping the specimen horizontally under a definite tension (1 kg.). The load is applied to the center of the strip transversely by a plunger moving in a vertical plane. The stretch is indicated by a scale showing the distance traveled by the plunger before the strip is broken.

The stretch, as measured above, is not a true strain measurement, since it measures the elongation of the paper up to the instant of complete fracture of the paper. This includes the elastic and the inelastic stretch of the paper, as well as the small distance through which the strip elongates while the ruptured paper is being pulled apart. In spite of its limitations, stretch is a reasonably good measure of the toughness of paper. It is a factor in the bursting strength and initial tearing resistance of paper. Stretch is important in twisting papers, toweling, tissues, cable wrapping papers, corrugating papers, and other similar grades which are folded or subjected to stress during use. The stretch is generally higher in the cross direction than in the machine direction of the paper. It is increased by increased beating of the stock used in making the paper. Paper tends to lose stretch on aging, and the loss in stretch on aging has been suggested as a better indication of the resistance of the paper to aging than the more commonly used fold test.

Bursting Strength

Bursting strength is a highly empirical test which is defined as the hydrostatic pressure required to rupture paper when deformed in an approximate sphere 1.20 in. in diameter at a controlled rate of loading. Pressure is applied to the paper at an increasing rate by pumping glycerine under the rubber diaphragm at a constant rate of 95 cc. per minute. The pressure is transmitted to the paper by the rubber diaphragm through a circular orifice which causes the paper to expand into an annular clamp holding the sheet against the orifice. During the period of the test, the paper must be securely clamped around the periphery of the test area to prevent slippage, because slippage increases the curvature and area under test which increases the pressure required to rupture the paper.

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[64] Clark Stretch Tester made by Thwing-Albert Instrument Co., Philadelphia, Pennsylvania

The pressure at the time of rupture is recorded on a sensitive, maximum-reading pressure gage. The reading includes the pressure exerted by the rubber diaphragm, as well as that of the specimen, and since this varies with the amount of expansion of the paper, it constitutes an uncontrolled variable. According to Clark,[65] the bulge of the rubber diaphragm at the time of rupture varies from 2 mm. for news to over 4 mm. for manila (with a bulge of 3 mm. corresponding to about 1.5 lb. on the tester). There are three bursting strength instruments, the Cady, the Mullen, and the Ashcroft.

The results obtained on the bursting strength tester depend upon the rate at which pressure is applied so that it is best to use motor-driven models which apply pressure at a controlled rate. Increasing the rate of loading tends to increase the reading because it increases tensile strength, which is a component of bursting strength. Other factors which affect the bursting strength are clamping pressure, presence of air in hydraulic system, calibration of pressure gage, and sharpness of edges of orifice.[66] Expansivity of the pressure gage and trapped air have the effect of reducing the pumping rate, which tends to lower the bursting strength reading.[67, 68] Individual readings should not be less than 25% or more than 75% of the total capacity of the gage. Routine calibration of the tester can be done by using standardized aluminum foil, which is available in strengths of 15 and 40.[69]

Bursting strength is recorded on the pressure gage in pounds, but the results are generally expressed as points. The results are sometimes reported as points per pound (sometimes called the burst ratio) obtained by dividing the bursting strength by the basis weight in pounds using the basic ream size. Sulfite bond paper usually runs around 1½ points per pound, mimeograph around 1 point per pound, and book papers around 0.25 to 0.50 point per pound, depending upon the amount of filler in the paper. Another way in which bursting strength is reported is as burst factor, which is obtained by dividing the bursting strength in grams per square centimeter by the basis weight in grams per square meter. The United States Government Printing Office has the following minimum specifications for the bursting strength of bond paper:

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[65] J. d'A. Clark, *Paper Trade J. 93,* No. 19: 207–210 (Nov. 5, 1931)

[66] R. C. McKee, C. H. Root and L. R. Ayers, *Tech. Assoc. Papers 31:* 343–364 (1948)

[67] F. T. Carson and F. V. Worthington, *Bur. Standards J. Research 6:* 339 (1931)

[68] N. G. M. Tuck and S. G. Mason, *Pulp Paper Mag. Canada 50,* No. 3: 132–141, Convention Issue (1949)

[69] These can be obtained from Hurlbut Paper Co., South Lee, Massachusetts

Weight (17 × 22—500)	13	16	20	24
Chemical wood bond	19	24	30	36
25% rag bond	22	28	35	42
50% rag bond	26	32	40	48
75% rag bond	29	36	45	54
100% rag bond	..	45	55	65

Bursting strength is a complex function of tensile strength and stretch. The stress is largely one of tension resulting from a pressure differential across the sheet at the time of rupture. The strain is approximately equal in all directions, thus building up unequal stresses in the paper. The fact that paper ordinarily ruptures in a line which is at right angles to the machine direction is primarily due to the fact that the paper has a low stretch in the machine direction which directs the stress caused by the bulging rubber diaphragm into a machine direction tension. By using a special plate with a narrow oblong opening which fits over the upper aperture of the ordinary Mullen tester, it is possible to measure a modified tensile strength using the Mullen tester.[70, 71]

According to Carson[72, 73] bursting strength is related to tensile strength by the following formula:

$$PR = 2T$$

where P is the bursting pressure, R is the radius of curvature of paper at rupture, and T is the tensile strength in machine direction per inch of width. Since R, the radius of curvature, depends upon the stretch of the paper, nothing is measured by the bursting test which cannot be determined by the tensile tester.[74] Using the above relationship, Roberts[75] and Owen[76] have shown that tensile strength can be calculated fairly well from ordinary Mullen values. In making calculations using the above formula, values for R can be obtained from stretch using relationships in Table IX suggested by Campbell.[77] In substituting in the formula, tensile strength should be expressed in pounds per inch of width, and bursting strength in pounds. The

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[70] M. Owen, *Pulp Paper Mag. Canada 50*, No. 3: 161–163, Convention Issue (1949)

[71] D. Roberts, *Pulp Paper Mag. Canada 43*, No. 10: 762–764 (Sept., 1942)

[72] F. T. Carson and F. V. Worthington, *Bur. Standards J. Research 6*, No. 2: 339–353 (Feb., 1931)

[73] F. T. Carson and F. V. Worthington, *Paper Mill 53*, No. 8: 136–142 (Feb. 22, 1930)

[74] F. T. Carson and F. V. Worthington, *Paper Mill 53*, No. 8: 126, 129, 140 (Feb. 22, 1930)

[75] D. Roberts, *Pulp Paper Mag. Canada 43*, No. 10: 762–764 (Sept., 1945)

[76] R. M. Owen, *Pulp Paper Mag. Canada 50*, No. 3: 161–163 Convention Issue (1949)

[77] W. B. Campbell, Forest Products Laboratories of Canada, Pulp Paper Lab., *Quarterly Rev.* No. 16: 1–3 (1934)

relationship appears fairly valid for machine-made papers, but not valid for laboratory handsheets.[78]

TABLE IX

CONVERSION TO VALUES OF R FROM STRETCH

Stretch, %	R, inches
0.52	3.44
1.12	2.32
2.04	1.75
3.22	1.42
4.70	1.20
6.47	1.047
8.58	0.934
11.05	0.848

The bursting test is one of the oldest tests and is widely used for routine mill control and for specification testing because of its simplicity. There has been considerable criticism of the bursting test as a measure of paper quality because (*1*) it is not a fundamental test and (*2*) it makes no distinction between the cross direction and machine direction strengths, or between the wire and felt sides of the paper. Despite its many disadvantages, however, the bursting test is still widely used. As a general rule, bursting strength follows the tensile strength, but it is also affected by the amount of stretch in the paper and, as such, is an indication of the give or toughness of the paper.

Sapp and Gillespie[79] have shown that during the drying of commercial papers, it is possible for the paper to lose bursting strength while gaining in tensile strength if the per cent elongation is decreased sufficiently by tension on the wet sheet. Figure VIII-2, taken from work of Sapp and Gillespie,[80] shows that the bursting strength diminishes approximately as a straight line function of the amount of stretching of the paper during drying, whereas the tensile strength goes through a maximum under the same conditions. Cottrall and Gartshore[81] found that uni-directional tension during drying reduces the strength to a much greater extent than tension applied equally by drying on glass plates. By applying weights of 850 g. to 4½-in.-wide strips of kraft paper made in the laboratory, the shrinkage during drying was reduced to zero and the bursting strength was reduced by 25 to 35%.

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[78] W. B. Campbell, Forest Products Laboratories of Canada, Pulp Paper Lab., *Quarterly Rev.* No. 16: 1–3 (1934)

[79] J. E. Sapp and W. F. Gillespie, *Paper Trade J. 124*, No. 9: 120–123 (Feb. 27, 1947)

[80] *Idem.*

[81] L. G. Cottrall and J. L. Gartshore, *World's Paper Trade Rev.* (Oct. 6 through Nov. 24, 1944)

Two factors are responsible for bursting strength, fiber length and interfiber bonding. Increased fiber length makes for a higher bursting strength, but bursting strength is even more affected by fiber bonding. Increased beating increases the bursting strength over most of the range, although a decrease occurs with excessive beating. Part of this loss in bursting strength on beating can be attributed to disintegration of the fiber, but since the bursting strength is also lowered when the sheet is increased in density by increased wet pressing (see Fig. XVI-3), at least part of the loss in burst must be attributed to a loss in stretch. Bursting strength is predominantly an internal sheet property, although it is influenced to some extent by surface sizing. Drying conditions on the paper machine have a definite effect on bursting strength as already pointed out.

Bursting strength is directly related to the utility of bag and wrapping papers and boxboards where the paper is subjected to a stress similar to that exerted in the bursting test. However, for most papers, there is no direct correlation between the bursting strength and the utility of paper.

Internal Tearing Resistance

The internal tearing resistance is measured on a pendulum type instrument (Elmendorf tear tester) which measures the amount of work done in tearing the paper through a fixed distance after the tear has been started by means of a cutter attached to the instrument. The specimen (2.5 in., 63 mm., in width) is clamped between two clamps, one of which is stationary and the other of which is attached to the pendulum. An initial slit is cut in the specimen, leaving 1.69 in. (43 mm.) of the paper to be torn by the instrument. The pendulum is released, and the specimen is torn in two as the clamp in the pendulum moves away from the fixed clamp. As the paper is torn, work is done on it. The work done in tearing is measured by the difference in potential energy of the pendulum at the beginning and end of the swing. Since the pendulum would swing to the right to an angle equal to the initial displacement angle (70°) if it were not for the dampening resistance of the paper, the final displacement angle can be taken as a function of the difference in potential energy of the pendulum or of the work done in tearing the paper. The angle is measured by a pointer mounted on the same axis as the pendulum which has a constant friction just sufficient to stop it at the highest point reached by the swing of the sector when there is no paper in the tester. During the period of the test, this friction pointer is held in place by a stop so that the scale swings past it during the tear.

Dividing the work done in tearing paper by the distance torn, which is constant for all tests, gives the average tearing force required to tear the paper. The scale attached to the pendulum is graduated from 0 to 100 and reads the ratio of work done (in gram-centimeters) to the total tearing length in centimeters of 16 sheets (i.e., 137.6 cm.), thus giving the force directly in grams. The scale readings on the instrument are intentionally made one-sixteenth of the actual values in order to have a convenient factor for converting the results when several sheets are torn at one time. Thus, tearing resistance as usually reported is the average force in grams required to sustain a tear on a single sheet of paper. Because the scale indicates one-sixteenth of the actual force in grams required to tear the sheets clamped in the tester, the force to tear a single sheet is calculated by multiplying the reading on the scale by 16 and dividing by the number of sheets tested.

Tearing resistance is sometimes reported as tear factor by dividing the tearing resistance in grams (per single sheet) by the basis weight in grams per square meter. It is also reported as tear ratio, or tearing strength in points (grams) per pound. The results obtained on strips torn in the machine direction are reported as tearing resistance in the machine direction, and results obtained on strips torn in the cross direction as tearing resistance in the cross direction. Machine direction tearing resistance is generally less than cross direction tearing resistance.

The standard procedure should always be carefully followed in making tear tests in order to keep to a minimum the additional work not directly involved in making the tear (e.g., work in bending the paper, and work involved in rubbing together of the edges of the torn paper). In making the test, a sufficient number of sheets should be chosen to obtain a reading between 20 to 60. Two, four, eight, or sixteen sheets can be used. A single sheet should never be used, since a reading obtained on a single sheet is never the same as a reading obtained on several sheets (even after the results have been corrected by multiplying by 16 and dividing by the number of sheets tested). If the line of tear deviates more than 10 mm. from the line of the initial slit, the results should be discarded. Splitting of the paper often occurs in making the test, particularly with papers of high tearing resistance. When splitting occurs only occasionally, it is advisable to throw out results obtained on the split specimen, but if a large number of tests show splitting, they should all be included in the average.[82] Some papermakers attempt to judge tearing resistance by hand. Hand tearing differs from tearing on the tear tester in that hand tearing applies the load at a much lower rate.

In general, the force required in tearing paper is much less than the force necessary to break a strip of the paper. The work involved in tearing consists of two components, work involved in pulling fibers out of the paper and work involved in rupturing the fibers.[83] The tearing resistance of paper made from unbeaten pulp is almost entirely due to work involved in overcoming the frictional resistance of the fibers being pulled from the paper. There is practically no tearing of the fibers, and since the total area of fiber contact is small, the frictional resistance is small and the tearing resistance is low. After a slight amount of beating, interfiber bonding is increased and the tearing resistance is greater because of the increased frictional resistance in pulling fibers out of the paper. This increase in tearing resistance in the early stages of beating is typical of most pulps. However, dried pulps do not always show this initial increase in tear, and pulps beaten in the laboratory sometimes do not show an initial rise in tear because of the relatively uniform beating treatment which decreases average fiber length about as rapidly as cohesiveness is increased.[84] As beating is greatly increased, the fibers no longer slip past one another readily, and consequently there is an increase in the number of fibers which are ruptured in tension. The action becomes more nearly a shearing action than a pulling action, and since the work involved in rupturing a fiber is much less than the energy involved in pulling a fiber out of the sheet, the energy required to tear the sheet decreases.[83] Stated differently, the sheet increases in cohesion and stiffness as a result of beating, and this tends to concentrate the tearing force into a smaller area, with the result that lower tearing values are obtained. This explains why tearing resistance steadily decreases upon beating after an initial increase. The effect is not due to loss of fiber length, since the same progressive loss in tearing resistance is obtained by adding increasing amounts of cementing agents (e.g., starch) to the stock, or by increasing the density of the paper by wet pressing (see Fig. XVI-3).

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[82] S. D. Wells, *Paper Trade J. 76,* No. 26: 248–251 (June 28, 1923)

[83] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 118,* No. 5: 13–19 (Feb. 3, 1944)

Tearing resistance is directly related to fiber treatment, and when taken in combination with the tensile or bursting strength, it furnishes considerable information on the manner in which the stock has been prepared. As a rule, tearing resistance varies inversely with bursting strength and density. If the tearing strength is very high and the bursting strength is very low, it may be taken as evidence that the pulp is insufficiently beaten. If the tearing strength is low and the burst very high, the pulp has probably been overbeaten. If tearing strength is disproportionately low in comparison with the burst, it can be taken as evidence of too much fiber cutting during fiber treatment since, for a given fiber furnish, the tearing resistance is a highly satisfactory measure of the amount of fiber length reduction brought about by refining. Tear resistance and stiffness (as measured on the Gurley) vary inversely.[85]

Fiber length is a very important factor in tearing strength. Tearing resistance increases with an increase in fiber length, because increased fiber length means an increase in the frictional drag work per fiber. Clark[86] states that tearing strength is increased according to the square root of the cube of the average fiber length (see Ch. VII). Southern kraft pulps made from pine and pulps made from western woods have a higher tearing resistance than northern kraft pulps made from spruce because of their greater fiber length. Tearing resistance is undoubtedly affected by the stress-strain properties of the individual fibers, a relationship which has been definitely established in the case of cotton fabrics.[87]

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[84] J. d'A. Clark, *Paper Trade J. 104,* No. 8: 118–120 (Feb. 25, 1937)
[85] C. A. Minor and J. E. Minor, *Paper Ind.* (Apr., 1935). (Taken from reprint.)
[86] J. d'A. Clark, *Paper Trade J. 115,* No. 26: 328–334 (Dec. 24, 1942)

Tearing resistance is higher on unstrained paper than on strained paper because of the extra work required to straighten out the fibers in unstrained paper (see Fig. XVI-10). Mason[88] points out that high tearing resistance is obtained with papers having a high creep, since creep tends to distribute the load over a wide area of the sheet. This explains why, on wetting of the paper, loss in tearing strength is not great compared with the great loss in tensile strength which occurs under the same conditions. The tearing resistance of creped paper is higher than that of uncreped paper because of the extra work involved in tearing the greater length of paper.

The tear test is particularly useful in the evaluation of bag, tag, wrapping, building, tissue, certain grades of boxboard, and other grades of papers which are subject to tearing strain in use.

Edge Tearing Resistance

From the standpoint of utility, the initial tearing resistance, which is the moment of force required to start the tear at the edge of the paper, is probably more important than the internal tearing resistance, which is the average force required to sustain the tear once it is started.[89] There is often considerable difference between the edge (initial) tearing resistance and the internal resistance, as shown by cellophane, which has a very high edge tearing resistance and a very low internal tearing resistance.

The initial tearing resistance is determined by the tensile strength and the stretch of the paper. Initial tear can be measured in the tensile tester using a special clamp with a V-notched beam which tears the sheet simultaneously at both edges of the strip. In this method of testing, a strip of paper 0.59 to 1.00 in. in width is threaded under a thin V-notched steel beam and both edges of the strip fastened in the upper clamp of the tensile tester. The load is applied slowly at first, and then at sufficient rate to tear the specimen in five to fifteen seconds. The results are reported for both the machine direction and cross direction of the paper.

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[87] O. B. Hager, D. D. Gagliardi and H. B. Walker, *Text. Research J. 17*, No. 7 (July, 1947)

[88] S. G. Mason, *Pulp Paper Mag. Canada 49*, No. 3: 207–214, Convention Issue (1948)

[89] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 118*, No. 5: 13–19 (Feb. 3, 1944)

The tensile tester can also be used to measure a combination edge tear and tensile strength by offsetting the test strip in the tensile tester at a definite angle so that most of the tension is applied to one edge of the strip. This test has been said to correlate fairly well with performance of the paper in web printing where breaks are often caused by uneven tension on the paper.

Folding Endurance

Folding endurance is an empirical test which measures the amount of folding the paper will endure before its tensile strength falls below a standard value of 1 kg. There are two instruments commonly used for measuring folding endurance, the Schopper (a German instrument) and the M.I.T. (developed by the Massachusetts Institute of Technology). There is no consistent relation between these two instruments.

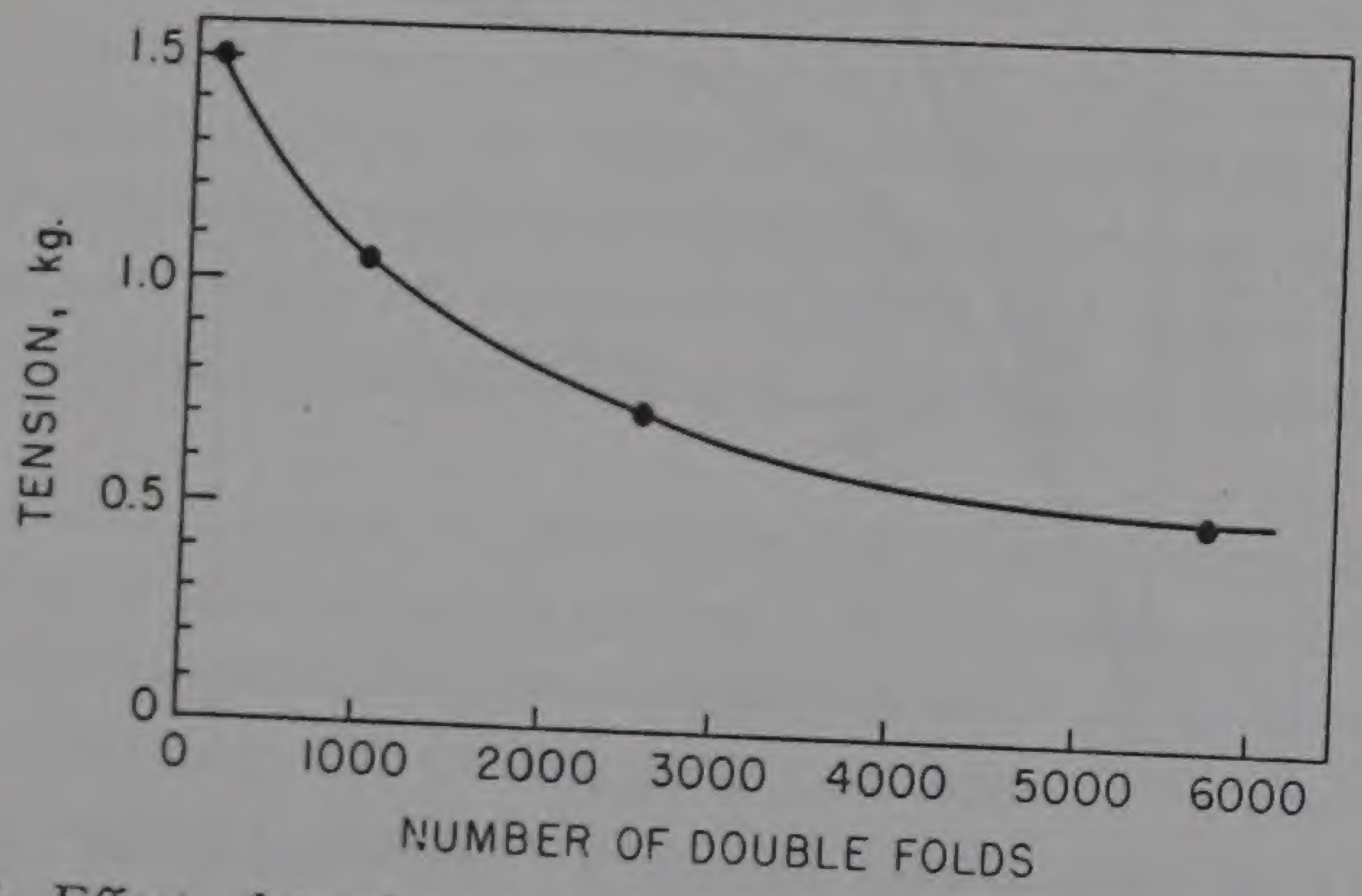

Fig. XVI-13. Effect of tension on test strip on folding endurance (rag paper).

In the Schopper, a strip of paper (10 cm. in length and 15 mm. in width) is fitted in a slotted blade and clamped at both ends under spring tension. The paper is then folded back and forth between four creasing rollers at a rate of about 120 double folds per minute. The tension varies from 790 g. to 1,000 g. during the period of the test, depending upon the position of the sample. The effect of variation in tension in the Schopper instrument is shown in Figure XVI-13 for an all-rag bond.[90] In making folding tests, the strips of paper must be inserted so that they are free of buckling or waviness, and the instrument should be in good adjustment so that the wear is even. Specimens can be removed just prior to breaking to determine the evenness of wear.

In the M.I.T. tester, the test strip is clamped between a spring-loaded clamp and an oscillating folding head. The oscillating head folds the paper to the right and left through a total angle of 270° at a rate of about 175

[90] L. W. Snyder and F. T. Carlson, *Paper Trade J. 96*, No. 22: 276–280 (June 1, 1933)

double folds per minute. The M.I.T. is a more versatile instrument than the Schopper, since the latter is limited to papers having a thickness no more than 0.01 in., whereas the M.I.T. will handle papers of widely varying thicknesses by using different jaws. The results obtained on the M.I.T. tester are affected by the curvature of the folding edges so that each new jaw should be standardized before installation.

Folding endurance is reported in double folds. Results obtained on strips cut with the machine direction lengthwise are reported as machine direction folding endurance, and results obtained on strips cut with the cross direction lengthwise are reported as cross direction folding endurance. As a rule, machine direction folding endurance is higher than cross direction folding endurance, although the reverse is sometimes true. The fact that cross direction folding endurance sometimes approaches or even exceeds machine direction folding endurance, in spite of the higher tensile strength in the machine direction, indicates that some flexibility or flow property is involved in the folding test. Mason[91] believes that high folding endurance is obtained with papers having a high rate of stress relaxation and relatively high primary creep. Rance[92] believes, on the contrary, that folding endurance bears a highly consistent relation to the elastic flexibility of the paper-measured on the stress-strain curve as line *DB* in Figure XVI-14. In this curve, line *ODA* represents the elastic spring line which would be the stress-strain curve in the absence of plastic flow. Thus, *OC* is a measure of the total elastic strainability, and *CE* the measure of plastic flow. Line *DB* is used in place of line *OC* to compensate for the permanent tension on the sheet in the fold tester.

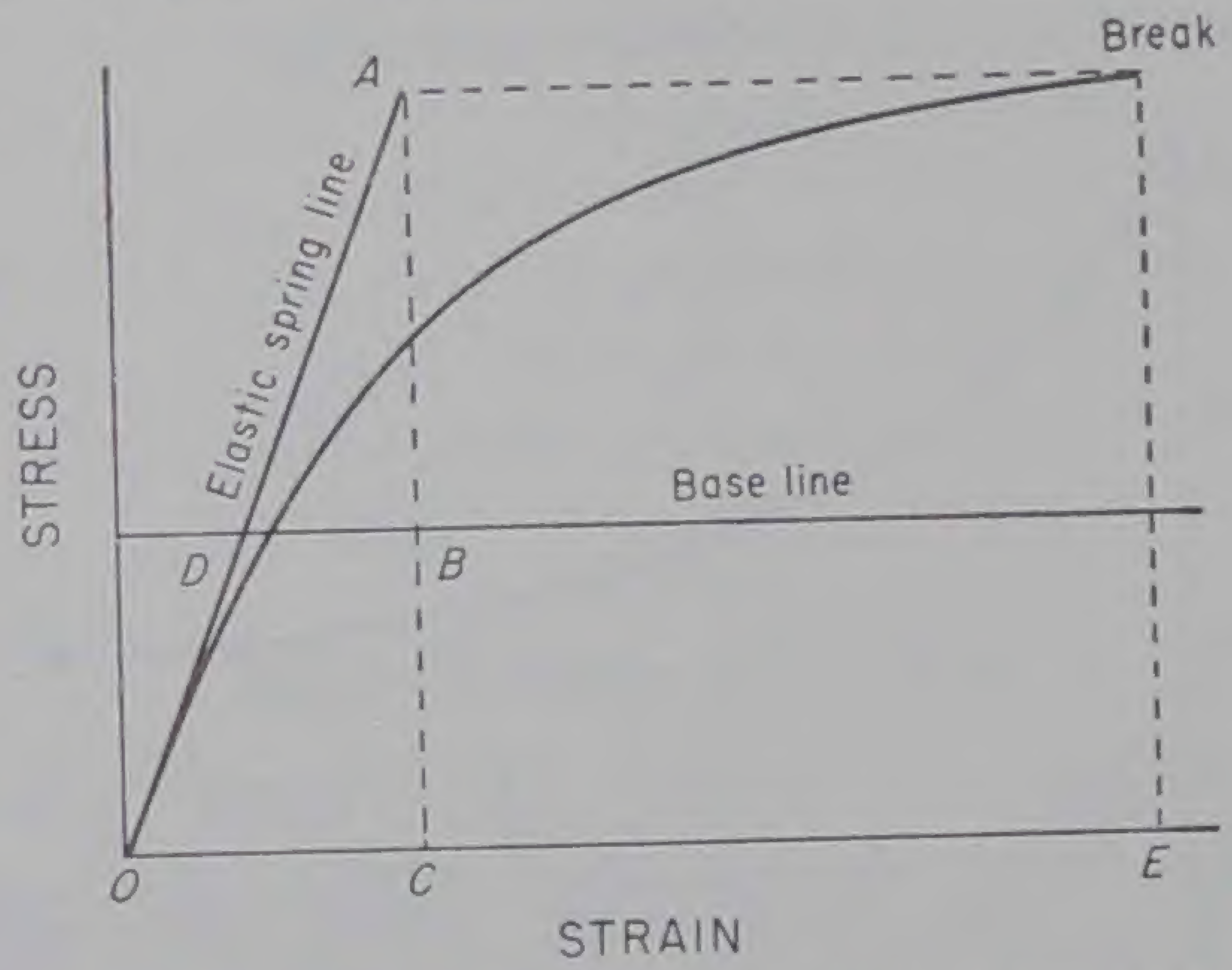

Fig. XVI-14. Stress–strain diagram for indicating folding endurance.

Folding endurance is, in a sense, a modified tensile strength determination, but the results are greatly affected by the flexing ability of the paper. As a rule, folding endurance follows tensile strength in the early stages of beating, but then falls off more rapidly than tensile strength, and eventually decreases with increased beating or wet pressing (see Fig. XVI-3), due to the paper becoming more brittle. Lack of adequate folding endurance can be the result of lack of fiber length, inadequate fiber bonding, or brittleness. Improper beating or poor formation are causes of poor folding endurance. Too much surface size (starch or glue) or too much beater starch tends to reduce folding endurance because of excessive brittleness of the fibers. Folding endurance is greatly affected by the moisture content of the paper, more so than the other physical tests (see Fig. XVI-35). Plasticizers increase the folding endurance of glassine papers by reducing the stiffness.[93]

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[91] S. G. Mason, *Pulp Paper Mag. Canada 49*, No. 3: 207–214, Convention Issue (1948)

[92] H. F. Rance, *Paper-Maker*, Midsummer Issue, 23, 32, 49, 50, 51 (1949)

As a rule, rag pulps produce papers of high folding endurance. On the other hand, groundwood papers, papers containing hardwood fibers, and coated or heavily filled papers have poor folding endurance. Mixtures of pulps do not always produce the expected folding endurance. Mixtures of rag and sulfite produce papers having folding endurance approaching the average of the two pulps, but mixtures of sulfite and wood filler pulps produce papers having a folding endurance only slightly above that of the weaker pulp.[94]

The general acceptance of the folding test is based upon the fact that it is the best means of measuring the quality of those papers which are required to resist considerable handling and folding in use. It is of particular importance in measuring the quality of high-grade sulfite and rag content bond, ledger, currency, index, cover, and record papers. The machine direction folding endurance of bond papers at 65% relative humidity generally varies from about 50 double folds for light-weight sulfite bonds to 3,000 or more double folds for heavy-weight rag bonds. The U. S. Government Printing Office specifies the values given in Table X as the minimum for the average double folds in each direction of bond and ledger papers.

Folding endurance is of value for indicating the utility of bag and box lining papers and for folding boxboards which are to be scored and folded into boxes. Boxboards are often tested by folding flat between the fingers, once in each direction, and with, across, and at an angle of 45° to the grain. The board is considered a bender if there is no break in the surface fibers. A scoring rule and creaser are sometimes used. Creasing with the grain is a more severe test than creasing across the grain; creasing diagonally across the grain is the most severe test of all.

One characteristic of the folding test is that the results vary widely.

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[93] N. R. Pike, *Paper Trade J. 102*, No. 5: 63–66 (Jan. 30, 1936)

[94] C. G. Weber, M. B. Shaw and M. J. O'Leary, *Paper Trade J. 117*, No. 13: 147–152 (Sept. 23, 1943)

TABLE X

Minimum Folding Endurance for Bond and Ledger Paper for U. S. Government Printing Office

	Bond			
Weight (17 × 22—500)	13	16	20	24
Chemical wood pulp bond	50	80	80	80
50% rag bond	100	150	150	150
100% rag bond	...	800	1000	1200

	Ledger					
Weight (17 × 22—800)	24	28	32	36	40	44
Sulfite ledger	...	80	100	...	125	...
50% rag ledger	150	150	150	200	300	300
100% rag ledger	1000	1000	1000	1200	1500	1500

The question often arises as to how much of the variation is due to test procedure and how much to variability of sample. In a study of the folding test, Reitz and Sillay[95] found that the coefficient of variation (standard deviation expressed as a percentage of the average result) varies for different grades of paper, but that the coefficient remains fairly constant from batch to batch of the same paper, and is independent of the machine and cross direction. They found that there is no greater difference between different models of the folding tester than would be expected as a result of test method variability, and that there is no appreciable difference in precision between the M.I.T. fold tester and the Schopper fold tester. Data obtained with both testers were in close agreement with normal distribution, as shown in Table XI. The expected reproducibility of results versus the number of tests made is shown in Figure XVI-15 for three different grades of paper taken from work by Reitz and Sillay. It can be seen from the curves that an unreasonable number of tests are required to obtain values within a few folds of the true average. For example, in the case of paper *A*, which has an average fold of 1,000, over 6,000 tests would have to be made to produce an average reproducible within 10 folds, at the 3σ assurance level (99.7%

TABLE XI

Showing Distribution of Data Obtained on M.I.T. and Schopper Fold Testers

Limits of standard deviations	Normal distribution	Actual fold data on M.I.T. tester	Actual fold data on Schopper tester
$\bar{X} \pm 16$	68.3	67.0	65.0
$\bar{X} \pm 26$	95.5	96.0	96.0
$\bar{X} \pm 36$	99.7	99.5	100.0

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[95] L. K. Reitz and F. J. Sillay, *Tech. Assoc. Papers 31:* 98–102 (June, 1948)

the time). Simmonds and Doughty[96] calculated that 3,648 tests would be required to obtain an average value of such accuracy that 99.7% (3σ) of all such averages would not differ from the true average (1,006 folds) by more than plus or minus 30 folds when the standard deviation of a single test is 604 (calculated from $n = (\sigma)^2/(\text{S.D.}_m) = (\sigma)^2/(m/3) = (604)^2/(30/3) = 3{,}648$ tests). Because of the variability of this test, folding endurance should not be used as a specification unless a tolerance of at least 20% is allowed for high-grade papers and 30% for ordinary grades.[97]

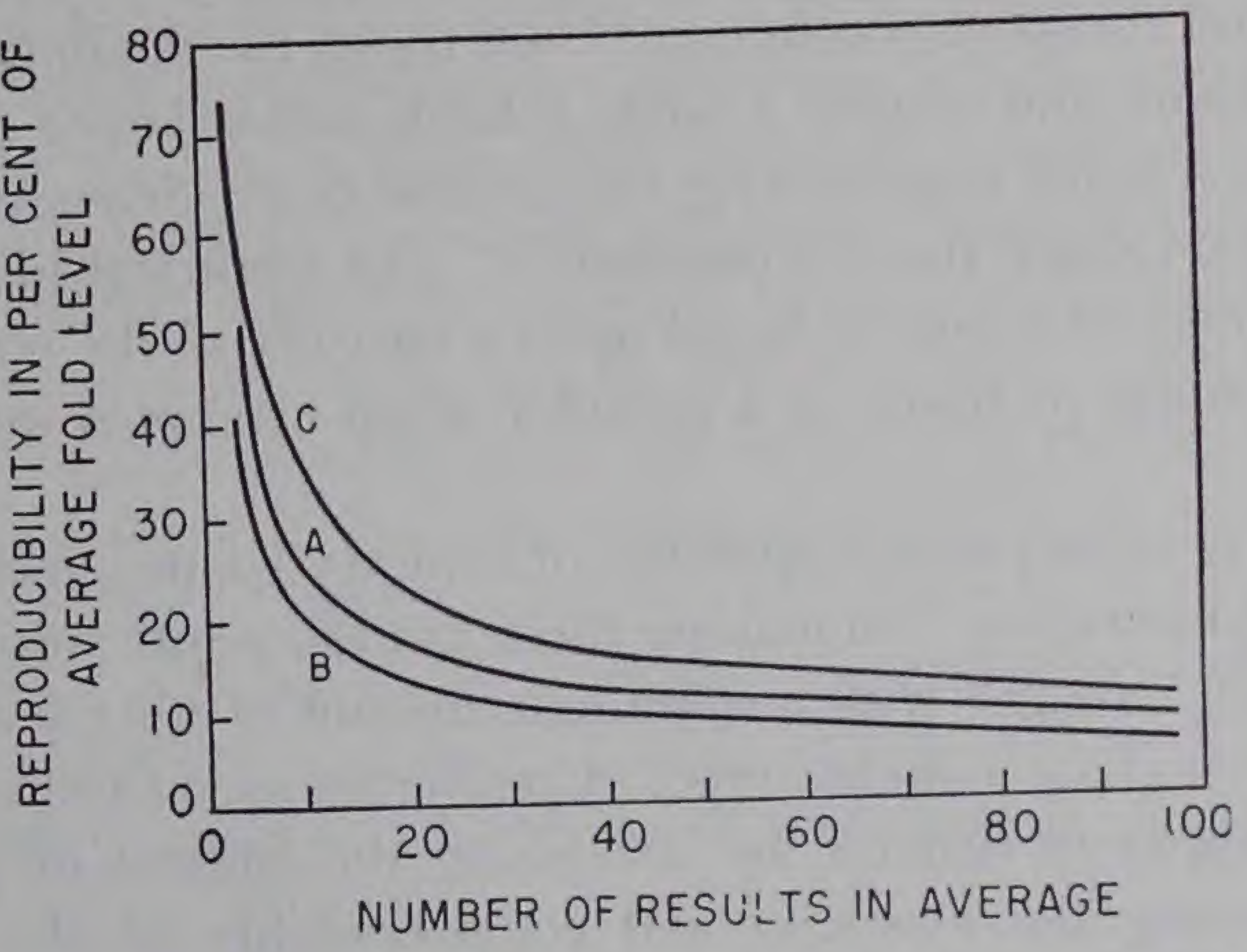

Fig. XVI-15. Reproducibility of fold test. Coefficient of variation: A paper, 26%; B paper, 21%; C paper, 35%.

Impact Strength

With the increased use of paper and paperboard products for structural purposes, the paper converter is showing more interest in direct physical measurement of the structural properties of paper. The use of rigidity tests has already been mentioned. Impact strength is another test which is being used to an increasing extent, particularly in the evaluation of fiberboards for building purposes.

Impact strength is a direct indication of the ruggedness of building board in use and is related to the ability of the board to resist dog-earing or breaking during handling. According to Lathrop and Naffziger,[98, 99] the impact strength of fiberboards can be greatly improved by the presence of long resilient fibers in the board. High impact strength is required in papers for resin-impregnated paper laminates.

[96] F. A. Simmonds and R. H. Doughty, *Paper Trade J. 97,* No. 25: 298–303 (Dec. 21, 1933)

[97] H. S. Spencer, *Tappi 32,* No. 7: 291–292 (July, 1949)

[98] E. C. Lathrop and T. R. Naffziger, *Paper Trade J. 127,* No. 27: 540–545 (Dec. 30, 1948)

[99] E. C. Lathrop and T. R. Naffziger, *Tappi 32,* No. 2: 91–96 (Feb., 1949)

Softness

Softness is the lack of harshness when paper is crumpled in the hand. (Softness is also used in opposition to hardness as evaluated by compressibility, as indicated in the following section.) The determination of softness by hand crumpling involves the appraisal of four main physical properties which contribute to the softness of paper, namely, density, rigidity, compressibility, and surface smoothness.[100] Of these, the flexibility of the paper is most important, and usually a fairly reliable indication of softness can be obtained from a value representing the inverse of rigidity multiplied by the log of the basic caliper times a constant.[100] An empirical method of measuring the softness of tissues is based upon a measure of the volume occupied by a given amount of tissue in a cylinder when crumpled under a definite load.

Softness is an important attribute of sanitary tissues, facial tissues, paper drapes, and toweling. In making these grades, a soft pulp is used which develops a high strength with a minimum amount of fiber bonding. These papers are often given a slight crepe. Creping increases the softness by decreasing the apparent density, by decreasing the amount of fiber bonding, and by increasing the elasticity and compressibility of the paper. Dry creping is generally more effective in reducing fiber bonding than wet creping. Softeners (glycerine, diethylene glycol, and diglycol stearate) are frequently added to the paper.

Hardness and Compressibility

Hardness is the property of paper which causes it to resist indentation by another material. Hardness is also used in reference to pulps to denote the degree of delignification. In a sense, these two properties are related, since a well purified pulp, that is, a soft pulp, will produce a soft, fluffy paper, whereas an undercooked pulp, that is, a hard pulp, will produce a relatively hard paper. Compressibility is defined as the reciprocal of the bulk modulus. It can be measured under static load by determining the change in caliper (or the change in volume) of the sheet at different pressures and expressing the results as a function of pressure.

The Bekk hardness tester measures elasticity and compressibility under dynamic load, but does not measure true hardness. The instrument consists of a ballistic pendulum equipped with a spherical steel surface which is struck against the surface of the test paper at a velocity of 1 meter per second. In carrying out the test, a thin film of ink is applied to the spherical striking surface. The diameter of the inked impression is used to calculate the depth of impression.

The Gurley-Hill Softness (S-P-S) test is a static test which measures the compressibility of the paper by the rate of flow of air between the paper and a flat metal plate containing raised metal plugs (0.002 in. high). Air is forced downward (by an inverted cylinder floating freely in a container partly filled with oil) through an open tube to the upper orifice plate against which the sample is clamped. In carrying out the test, the paper sample is punched and clamped in the tester on top of the special plate with the raised plugs. Pressure is applied by means of a lever arm, thereby forcing the metal plugs into the paper surface. The plugs are designed to allow air leakage between the two surfaces when no paper is inserted of 100 cc. per ten seconds. When paper is inserted, air leakage depends upon the softness of the paper, since the deeper the plugs are forced into the paper, the slower is the air leakage between the paper and the metal surface. Different weights can be used depending upon the softness of the paper under test. The small weight (0.34 lb.) gives a pressure of 300 p.s.i. on the plugs and the large weight (2.0 lb.) gives a pressure of 1,300 p.s.i. on the plugs. The test is appreciably affected by basis weight and smoothness of the paper.[101] The results are reported as time in seconds to leak 100 cc. of air. Soft papers give a higher reading than hard papers because of the longer time required for the leakage of the air.

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[100] L. M. Lyne, *Pulp Paper Mag. Canada 51,* No. 8: 80–84 (July, 1950)

The surface hardness of paper or paperboard can be measured by the abrasion test, the results of which correlate fairly well with the erasing properties of paper and the scuffing resistance of paperboard. The instrument used for making this test is called the Taber Abrader. It consists of a horizontal turntable and center clamp to which the specimen is attached, and two weighted arms equipped with special abrasive wheels. The abrasive wheels freely rotate on the specimen during the period of test and wear away the paper surface at a rate depending upon the wearing resistance of the paper. The speed of rotation of the turntable is 65 to 75 r.p.m., and the pressure applied by each arm varies from 500 to 1,000 g., depending upon the size of the weight used. Wheels of varying abrasive qualities can be used. After each 1,000 revolutions, the abrasive wheels must be resurfaced by running on a special abrasive disk. During the period of the test, accumulated dust should be removed with a brush. The results are reported as the abrasion loss in milligrams per 1,000 revolutions for a test surface of approximately 10 sq.cm. The results vary from about 100 mg. for well-beaten papers to 2,000 mg. or more for soft papers.

In general, hardness follows the density of the paper, and consequently papers requiring a high degree of hardness should be made from easy beating pulps. A high moisture content lowers the hardness of paper.

Hardness is one of the most important properties influencing the printing qualities of paper, since it affects the ease with which the printing plate establishes contact with the paper surface. In printing (notably letterpress printing), the softer the paper the better the contact with the printing plate (see Ch. XIX). Surface hardness is desired in some papers (e.g., boxboards and writing papers), and these are usually surface treated with starch or glue.

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[101] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 110*, No. 23: 303–309 (June 6, 1940)

Bulk and Bulking Thickness

Bulk is a measure of the thickness of a pile of a specified number of sheets under a definite pressure (usually 7–9 p.s.i.). Bulking thickness is the average thickness of a single sheet determined from the thickness of a stack of sheets. Bulking factor is obtained by dividing the bulking thickness by the basis weight. Bulk factor (bulk index) is the same as the apparent specific volume, i.e., the reciprocal of the apparent specific gravity.

Bulk is dependent upon the thickness and compressibility of the paper. The bulk of a stack of sheets will generally be less than the bulk calculated from the thickness of individual sheets due to the nesting and compacting which occurs on stacking. In general, bulking thickness is about 2 to 6% lower than the figure obtained from the caliper of a single sheet.

Bulk is of practical importance for printing papers to be bound into book or pamphlet form. There is a special grade of book paper, called bulking paper, which is made very bulky. To make this paper, soda, rag, or alpha pulps are generally used, the stock is beaten very little, no fillers are used, and special felts are used on the machine. The finish given to the paper is very important, as shown in Table XII giving the bulk of several different grades of printing papers in 60-lb. weights (25 × 38—500). Uniformity of bulk is an important property on all papers, since non-uniform bulk causes hard or soft spots in the paper roll.

TABLE XII

BULK OF PRINTING PAPERS OF DIFFERENT FINISH

Finish	Sheets to the inch
Antique	300
English finish	510
Supercalendered	640

Porosity

Paper is a highly porous material, as attested by its low specific gravity (0.5–0.8) compared with that of cellulose (1.5). Commercial papers contain as much as 70% air, which is due to (*1*) true pores, those openings which extend entirely through the sheet, (*2*) recesses, those openings connected to one surface only, (*3*) voids, those air spaces connected to neither surface. According to Baird and Irubesky,[102] the true pore volume of a typical paper is only 1.6% of the total air fraction, the remaining 98.4% being the recess and void volume. This explains why greaseproof paper which contains as much as 48% air volume[103] can still function effectively as a greaseproof barrier, since it contains practically no true pores. The recess volume is generally higher on the wire side of the paper than on the felt side.

The air volume of paper can be calculated as follows, but the air volume obtained in this way does not distinguish between pores, recesses, or voids:

$$\text{air volume} = 1 - \frac{\text{specific gravity of paper}}{\text{specific gravity of cellulose}}$$

Apparent density (obtained from the basis weight and thickness using the metric system) is generally used in place of specific gravity, since it is impossible to determine the specific gravity of paper by the displacement of water.

The pore volume of paper is generally expressed as equivalent pore radius, i.e., the radius of a single pore of length equal to the sheet thickness which would give the same flow as the average value for all the pores in a unit area of the paper. The pores in paper form a complicated system of interlocking, crooked, and criss-crossing channels which range in size from a fairly large diameter to capillary dimensions. Equivalent pore radius tells nothing about the size, shape, and distribution of the pores, but it is useful for comparing the porosity of different papers. Using an air permeability method and a modification of Poiseuille's equation,[104] Carson[105] found the average effective pore size to vary from 0.2 micron for coated book paper to 1.2 microns for bond paper. Simmonds[106] obtained values of 0.1 to 4 microns for blotting paper, using a capillary rise method.[107] Foote[108] obtained a value of about 0.19 to 0.35 micron for unsized bond paper using capillary rise, contact angle, and swelling measurements.

[102] P. K. Baird and C. E. Irubesky, *Tech. Assoc. Papers 13:* 274–277 (May, 1930)

[103] R. M. Cobb, *Paper Trade J. 100,* No. 16: 200–203 (Apr. 18, 1935)

[104] Formula used by Carson:

$$V \rightarrow \frac{n\pi r^4 \Delta P}{8\eta l}\left(\frac{2P-\Delta P}{2P}\right)\left(l+\frac{4S}{r}\right)$$

in which ΔP is the pressure drop through the paper, P is the applied pressure, S is the mean free path of the gas, n is the number of capillaries, η is the viscosity, r is the radius of the capillaries, and l is the length.

[105] F. T. Carson, *J. Research Natl. Bur. Standards 24,* No. 4: 435–442 (Apr., 1940)

[106] F. A. Simmonds, *Paper Trade J. 97,* No. 10: 40–42 (Sept. 7, 1933)

[107] The capillary rise method is based on the following equation:

$$h^2 \rightarrow \frac{r\sigma t}{2\eta}$$

where h is the height of capillary rise, t is the time, σ is the surface tension, η is the viscosity, and r is the radius of a uniform capillary that will give the same rise.

[108] J. E. Foote, *Paper Trade J. 109,* No. 14: 180–188 (Oct. 5, 1939)

In routine paper testing, porosity is generally measured by the resistance of a paper sample of given dimensions to the passage of air under standardized conditions of pressure, temperature, and relative humidity. The results are expressed in arbitrary units as the time taken for the passage of a given volume of air or as the amount of air passed in a given period of time. The flow of air through paper is directly proportional to the pressure difference (for small pressure differences), to the time of flow, and to the effective area of the specimen; it is inversely proportional to the thickness of the sample.[109] Air resistance varies inversely as the fourth power of the radius of the pores.[110] Two papers may have the same equivalent pore radius but different air resistance if the papers differ in thickness, since equivalent pore radius is independent of sheet thickness, whereas air resistance is dependent upon sheet thickness.[111, 112]

The air resistance of paper is commonly measured with the Gurley Densometer or the S-P-S Tester. These testers measure the time for the flow of a standard volume of air (usually 100 cc.) through a standard area (usually 1 sq.in.) of the paper under uniform light pressure. Air is forced through the paper by pressure resulting from the weight of the inner cylinder floating freely in an outer cylinder partly filled with light oil. In the densometer, the paper is clamped in the top of the inner cylinder, whereas the paper is clamped in the base of the S-P-S tester on top of a perforated plate. The instruments are equipped with an elastic rubber (Thiokol) gasket to prevent air leakage laterally across the surface of the paper. This gasket is part of the densometer, but must be inserted in the S-P-S tester when porosity tests are being made. The movable inner cylinder is graduated in units of 50 ml., and the volume of air transmitted is read on this gage. The time for the passage of 100 cc. of air is taken after the inner cylinder has been released and attained a steady downward movement. The apparatus should be tested periodically for leakage by testing a smooth, non-porous material such as metal foil: leakage should not exceed 10 ml. of air per hour.

The Williams tester uses a movable inner cylinder and an outer cylinder partially filled with mercury. The specimen is folded and perforated and then a small square of rubber (also perforated) is placed in the fold of the sample. The specimen is then placed between the rubber-faced clamps so that all four surfaces are sealed against escaping air. All air must then pass out through the paper in a line perpendicular to the plane of the paper.

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[109] F. T. Carson, *Paper Trade J. 99,* No. 11: 107–116 (Sept. 13, 1934)

[110] R. M. Cobb, *Paper Trade J. 100,* No. 16 (Apr. 18, 1935)

[111] R. H. Doughty, C. O. Seborg and P. K. Baird, *Paper Trade J. 94,* No. 24: 312–314 (June 16, 1932)

[112] R. H. Doughty, C. O. Seborg and P. K. Baird, *Paper Trade J. 95,* No. 13: 149–151 (Sept. 19, 1932)

Timing is controlled by a mercury column in a small tube in the front of the apparatus. An electric timer is started when the mercury is raised to the correct level at the start and is automatically shut off when the mercury has fallen, due to the air pressure being relieved.

Air resistance increases greatly with increasing solid fraction.[112] There is no absolute relationship between solid fraction and air resistance, however, since papers made from different pulps have different air resistance, even at the same solid fraction.[113] Air resistance generally decreases with increasing amounts of rosin size and filler, with the bulky fillers such as calcium carbonate causing the greatest decrease in air resistance. Lane[114] found that low percentages of fillers reduce the air resistance by reducing fiber bonding, but that high percentages of fillers increase the air resistance by plugging the sheet. Foote[115] found the average pore diameter to be greater in the machine direction of the paper than in the cross direction.

Air resistance measurements are commonly used as a control test for paper manufacture because of the indirect correlation between porosity and formation and strength of the paper. Porosity is of direct importance in writing and printing papers, since it is a factor in the absorption of inks. It is an important property of coating rawstock for pigment-coated papers where it affects the absorption of adhesive. It is definitely related to the oil resistance, and hence is an important property of greaseproof and oil-resistant papers. Albert[116] found a linear relation to exist between air resistance in the range of 10 to 150 seconds on the Gurley instrument and oil resistance, when the latter was measured by dividing the seconds for oil penetration by the thickness of the paper square (S/T^2). Porosity is an important property of unimpregnated electrical insulating papers because of its influence on the dielectric constant.[117]

Porosity is an extremely important property of saturating papers. However, because of the low air resistance (1–5 seconds) of many saturating papers, the conventional instruments are not well adapted for testing these papers. There is, however, a special permeometer for testing highly porous papers (e.g., filter, tissue, blotting, absorbent, and saturating papers) which measures air flow as small as 1 cu.ft. of air per minute per square foot at a pressure drop equal to 0.5 in. of water. This instrument uses a null method of measurement and is, in principle, a pneumatic bridge consisting of a reference chamber and a test chamber through which air is drawn simultaneously into a reservoir. The valve adjusts the suction in the test chamber

[113] R. H. Doughty, *Paper Trade J. 95,* No. 10: 111–118 (Sept. 8, 1932)

[114] W. H. Lane, *Paper Trade J. 117,* No. 3: 28–32 (July 15, 1943)

[115] J. E. Foote, *Paper Trade J. 109,* No. 14: 180–188 (Oct. 5, 1939)

[116] G. A. Albert, *Paper Trade J. 101,* No. 11: 127–131 (Sept. 12, 1935)

[117] L. Emanueli, *Technologie und Chemie der Papier- u. Zellstoff-Fabrikation 25,* No. 4: 49–51, (Apr. 28, 1928)

so that it balances the suction in the reference chamber, as indicated by a zero reading. The valve reading is used as a measure of the air permeability.

Porosity is very important in bag papers to be filled by valve connection where the bags must have a certain porosity to prevent bursting during filling. In cigarette papers, the porosity must be controlled through the use of filler (calcium carbonate) to regulate the burning rate. Anti-tarnish wrapping papers should be made with as low a porosity as possible in order to reduce the penetration of hydrogen sulfide, oxygen, carbon dioxide, and other gases which cause the tarnishing of steel, copper, and silver articles. Porosity is very important in filter papers used for the filtering of oils, aqueous fluids, and gases. Gas mask filter paper must be permeable to air, but impermeable to smoke and fume particles. Perot[118] found that the filtering of smoke by paper is primarily a mechanical effect which is dependent upon sheet density, sheet weight, and fiber diameter, but is independent of fiber length. Straw pulps mixed with cotton or coniferous wood pulps seem to work better in filter paper than wood or cotton pulps alone because of the small diameter of the straw fiber.[119]

Porosity, or more specifically, void volume, is of particular importance in insulating papers made from wood fibers, asbestos, or mineral wool fibers. The voids in the paper should be small so that circulation of air within the voids is held to a minimum. Some of the papers requiring a high void volume are sheathing papers used between the walls of homes to keep out the wind, felt papers used for heat insulation, and deadening felt used between the walls and underneath floors and carpeting to deaden sound. Another grade is insulating board used as lath, roof insulation, outside sheathing, acoustical tile, and for insulating walls. In making this type of heavy board, an attempt is made to strike a balance between the amount of long fiber material, which is used for the structural framework, and the amount of short fiber material, which is used as a filler or binding material. The usual proportion is 55 to 70% long free fiber, and from 30 to 45% short-fibered material. The fine material is derived from many sources, including corn stalks, bagasse, and groundwood. Southern pine is widely used for the long-fibered material. Recently, insulating board has been made from 100% pine groundwood pulp. The properties of insulation board are approximately[120] as follows: weight, 1¼ lb. per square foot; thickness, 1 in.; thermal conductivity, 0.33 B.t.u. per square foot per °F. difference per hour; density, 14 to 18 lb. per cubic foot. Another grade of wallboard, known as panel board or hardboard, is made with a relatively high percentage of short-fibered material in order to produce a board of greater density, rigidity, and better finish. This grade of board is frequently coated for use as inside decoration.

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[118] J. J. Perot, *Paper Trade J. 124,* No. 25: 278–286 (June 19, 1947)

[119] S. I. Aronovsky, G. N. Nelson and E. C. Lathrop, *Paper Ind. 29,* No. 9: 1300–1303 (Dec., 1947)

[120] C. G. Muench, *Paper Trade J. 125,* No. 5: 58–60 (July 31, 1947)

Smoothness

Smoothness is concerned with the surface contour or mechanical perfection of the paper surface. Optical smoothness of paper is discussed under finish and gloss.

Probably the most accurate method of measuring smoothness is by means of a microscope using a micrometer focusing adjustment by which the microscope is focused on a small area of the paper surface and the micrometer reading is noted. The paper is then moved to a small predetermined distance, the microscope again focused, and a new micrometer reading is noted. In this way, a complete and accurate picture of the paper surface is obtained, but the method is slow and tedious, and suitable only for research work.

Another direct means of measuring paper smoothness involves the tracing of surface irregularities, using a surface analyzer, so that a profile of the paper surface is obtained. Detector needles are used for contacting the paper surface.[121, 122] In one instrument, a steel ball is mounted on a tracer arm which automatically adds the total movement as the steel ball is moved over the surface of the paper. The Forest Products Laboratory roughness tester, which is also based on the tracer principle, uses a detector needle with a flat end. The needle makes intermittent contact with the paper surface to avoid side stresses and the plowing effect of continuous tracing, and thus the paper is essentially stress-free at the time of measurement of its roughness. The Brush surface analyzer magnifies and records the contour of the paper and indicates the average variation between the high and the low areas.

Recently Chapman[123] has described a modified version of the Davis tester[124] for measuring smoothness. In this method, the test sample is pressed against the lower surface of a glass prism and the sample illuminated by an approximately parallel beam of light passed through the prism at right angles to the surface of the paper. The amount of reflected light in the prism having an angle greater than 41° 8′ is taken as a measure of the sample in contact with the prism. The amount of this light is measured on a photoelectric cell and compared with the total light measured on a second photoelectric cell.

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[121] S. Way, *Mech. Eng. 59,* No. 11: 826–828 (Nov., 1937)

[122] M. Heinig and P. K. Baird, *Paper Trade J. 113,* No. 15: 195–200 (Oct. 9, 1941)

[123] S. M. Chapman, *Pulp Paper Mag. Canada 48,* No. 3: 140–150, Convention Issue (1947)

[124] M. N. Davis, U. S. Patent 2,050,486 (Aug. 11, 1936)

Routine measurement of smoothness is generally made by air flow instruments which measure the rate of flow of air across the surface of the paper. Air flow smoothness testers are based upon the principle that the volume of air voids between a paper and a plane surface is proportional to the roughness of the paper, and that the rate of air flow between these two surfaces is proportional to the volume of the air voids. In carrying out the test, the paper is clamped under definite pressure and the time taken for a given volume of air to flow either between the paper and a standard surface, or between two or more sheets of the paper. There are three principal air flow instruments used for measuring smoothness, Bekk, Williams, and Gurley. All are based on the same principle, but there is no constant relation between the three instruments.

In the Bekk smoothness tester,[125] the time is taken for a given volume of air (10 ml.) to flow under reduced pressure between the paper surface and a flat polished glass surface having an area of 10 sq. cm. The air passed between the two surfaces is conducted through a circular aperture in the glass surface into a vacuum chamber. A vacuum is maintained in the chamber by means of a mercury pump, a mercury manometer being used to show the difference between the pressure in the chamber and the atmospheric pressure. The paper is placed with the surface to be tested in contact with the polished glass and a rubber pad placed on the paper. A metal pressure disk is then placed on top of the rubber, and a pressure of 1 kg. per square centimeter is applied through this plate to the paper by means of a pressure bar. The air pressure in the chamber is then adjusted to 380 mm., and the time is taken for the pressure to drop to 360 mm., representing the passage of 10 ml. of air between the paper and the glass surface. Bekk smoothness values have proved to correlate fairly well with printing quality.[126] This test is widely used by government agencies.

In the Gurley tester, the paper is clamped between two optically flat metal surfaces having an effective area of 1 sq. in. Pressure is applied by an unweighted lever arm to place the paper under a pressure of 3 p.s.i., which is lower than the pressure used in the Bekk and is one of the reasons contributing to the lack of agreement between the two testers. Ordinarily, eight sheets of paper are tested at one time, which gives an overall, top-to-bottom average of sixteen surfaces in one reading. In carrying out the tests, the eight sheets are arranged so that all the felt and all the wire sides are in contact, and then a hole is punched through the pad of sheets. The test does not differentiate between top- and bottom-side smoothness, but instead gives an average of the two sides. The results are usually reported as the number of seconds required for 50 ml. of air to pass between the test surfaces of eight thicknesses of samples. The percentage average deviation of individual readings from the mean for Gurley S-P-S smoothness was found to be 6.4 for a number of different papers.[127] In the case of paperboards, smoothness may be tested in the S-P-S tester by placing two specimens (the top one having a hole punched in it) between two pieces of rubber (the top one having a hole in it). The paper surface to be tested should be placed in contact with the corresponding surface on the other specimen so that the air flows out between two similar paper surfaces.

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[125] Sold by A. v. d. Korput-Baarn (Holland)

[126] B. L. Wehmhoff, *Tech. Assoc. Papers 18*, No. 1: 337–339 (1935)

In the Williams tester, the air escape is between two paper surfaces, the other surfaces of the paper being in contact with rubber-faced clamps to seal off these sides of the sheet. In making the test, the specimen (at least 2 in. in size) is folded over so that the felt sides are in contact, the sample is punched with an ⅛ in. round hole and then is clamped in the tester at a pressure of 30 p.s.i. The results give felt-side smoothness, and the test must be repeated with the wire sides in contact to obtain the wire-side smoothness, using a new sample each time because of the compression of the sheet which occurs in the test. Results are usually reported as the number of seconds for the passage of 25 ml. of air between the surfaces of the test specimens. A correction is sometimes made in the results for the transverse porosity of the paper by taking readings with a thin rubber disk (having a hole in the center) inside the folded paper sample to seal off all four surfaces and thus measure only the escape of air laterally through the sheet structure. This porosity reading is then used to correct the smoothness reading, as follows:

$$\text{corrected smoothness} = \frac{\text{smoothness times porosity}}{\text{porosity minus smoothness}}$$

This correction is not always used, because the relation between smoothness and plane porosity remains reasonably constant for a given paper. Furthermore, some chemists do not feel that the correction is a legitimate one. In making smoothness tests with the Williams instrument, it is necessary to maintain a constant temperature, not only for the effect on the paper properties, but also to keep the air forced over the sample at a constant value.

As a rule, testers of the air-flow type are fairly well adapted to the testing of paper smoothness. There are, however, several shortcomings of this type of instrument. The results are more affected by a few large depressions than by an equivalent area of small depressions because the air flow is proportional to the fourth power of the surface channels.[128, 129] This places undue emphasis on accidental defects. The flow of air is affected by the depth of the cavities in the paper surface, which is often not indicative of the suitability of the paper for a certain purpose, for example, in printing, where very deep cavities are no more harmful to printing quality than medium-deep depressions.[130] On the other hand, the flow of air is not greatly influenced by discontinuous irregularities in the paper surface (e.g., wire marks), and these irregularities are often important in the use of the paper.[130] In the case of very smooth papers, such as coated papers, the readings obtained on air flow smoothness testers are principally a measure of transverse porosity, rather than smoothness, and are therefore affected by thickness and density of the sample.[131]

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[127] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 110,* No. 23: 303–309 (June 6, 1940)

[128] S. M. Chapman, *Pulp Paper Mag. Canada 48,* No. 3: 140–150, Convention Issue (1947)

[129] **Instrumentation Studies, *Paper Trade J. 104,* No. 13: 188–191 (Apr. 1, 1937)**

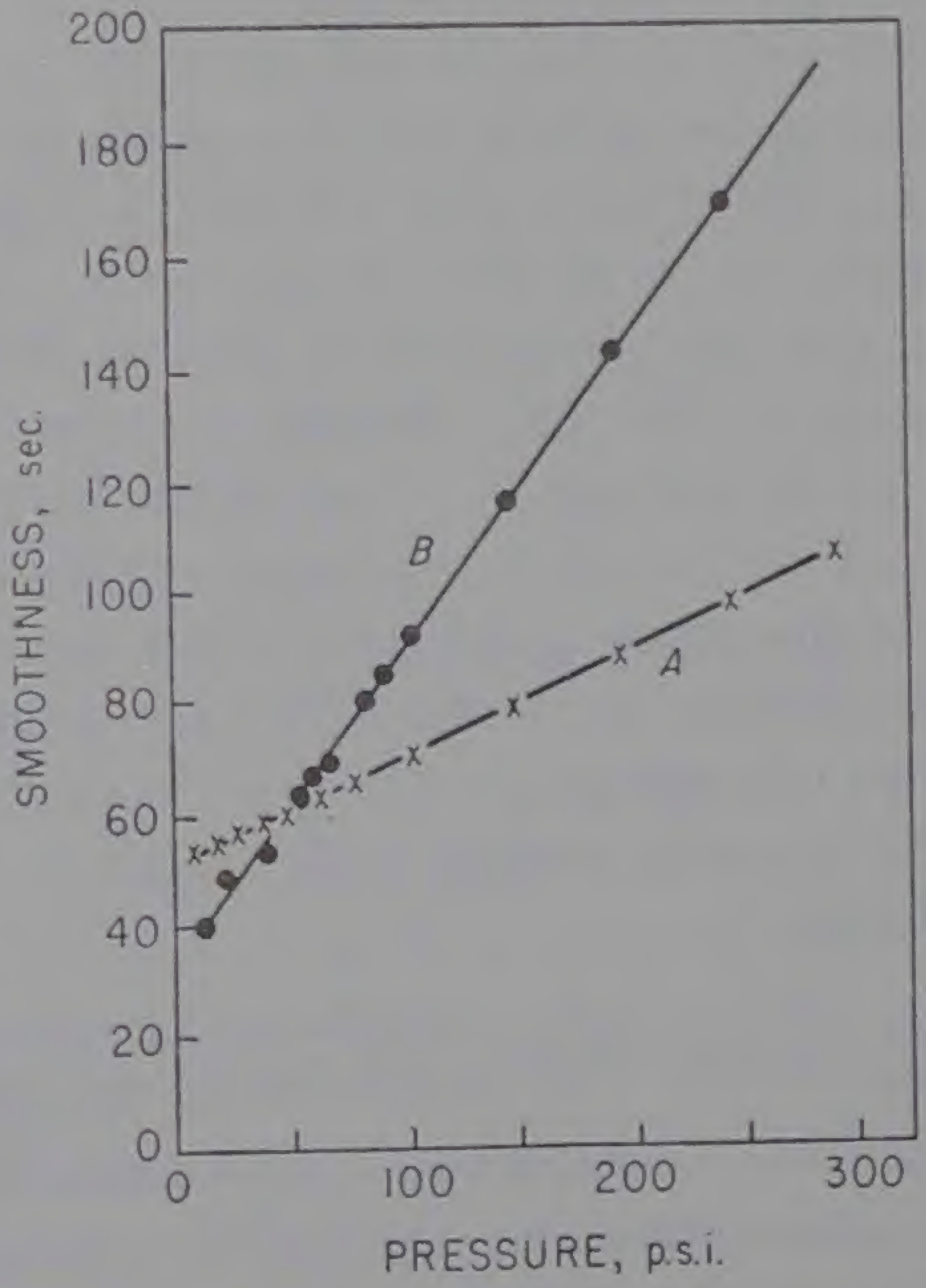

Fig. XVI-16. Effect of pressure on the smoothness of paperboard.

Smoothness is greatly affected by the pressure to which the paper is subjected at the time of testing, since increased pressure tends to level off the surface of the paper. In many cases, smoothness readings at low pressure are not indicative of smoothness at higher pressures, as illustrated in Figure XVI-16, which shows two samples of paperboard which have essentially the same smoothness at 50 lb. pressure, but markedly different smoothness at higher pressures.[132] In this case, board *B* printed more satisfactorily than board *A* because of its greater smoothness at high pressures. Increasing the gage pressure on the sample in the Williams tester from 10 to 60 p.s.i. increases the smoothness reading from ten to forty-five seconds.[133] Figure XVI-17, which was taken from work done by Chapman,[134] shows the effect of pressure on the smoothness of newsprint measured by the amount of surface contact between the paper and a piece of smooth glass. A high moisture content increases the smoothness under pressure, because the sheet is made softer and more easily flattened. The effect of relative humidity on the smoothness of the paper at various pressures is also shown in Figure XVI-17.

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[130] S. M. Chapman, *Pulp Paper Mag. Canada 48,* No. 3: 140–150, Convention Issue (1947)

[131] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 112,* No. 4: 34–38 (Jan. 27, 1938)

[132] J. F. Halladay, *Paper Trade J. 106,* No. 25: 341–350 (June 28, 1938)

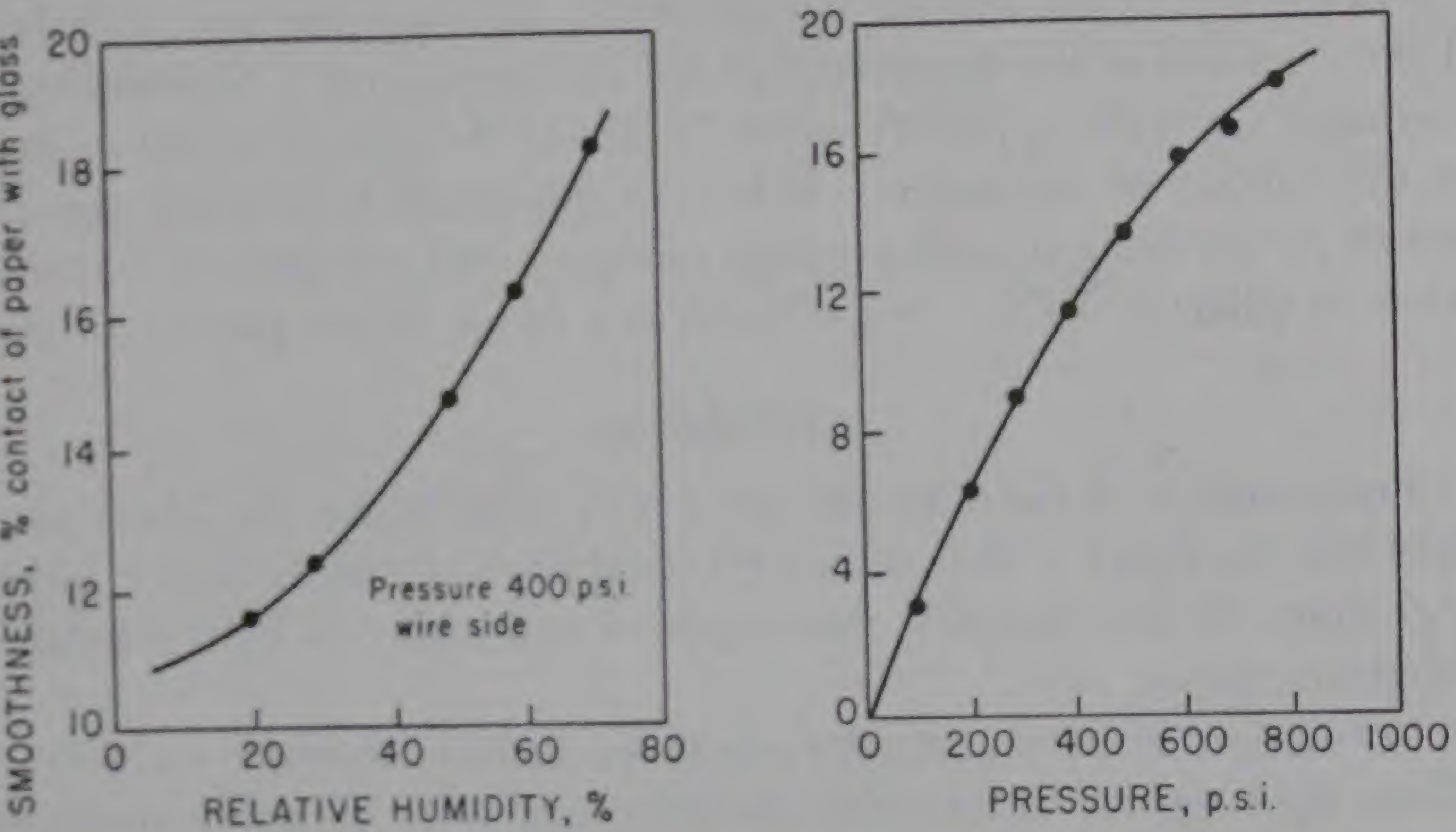

Fig. XVI-17. Effect of relative humidity and pressure on the smoothness of newsprint.

Increased beating of the stock increases the smoothness of the final paper. The shake on Fourdrinier machines is another important factor in improving smoothness. The type of wire and type and weave of the felts used on the machine also affect the smoothness. Increased wet pressing and increased calendering improve the smoothness, but in general, it is better to make the sheet smooth rather than try to calender it smooth. Calendering a rough paper so that it is smooth creates hard spots in the paper which tend to swell when the paper is wet (e.g., with aqueous coating mixtures). Most printing papers are, however, calendered to increase their smoothness. Filling improves the smoothness, particularly after calendering. Surface sizing improves smoothness, and pigment coating has a very definite effect on smoothness, particularly if the coated paper is supercalendered. The type of pulp has an important effect on smoothness. Groundwood pulps, as a rule, produce rough papers, because of the fiber bundles. Southern kraft pulps and some of the West Coast pulps produce rough papers because of the large size of the fiber. On the other hand, well-beaten spruce sulfite and rag pulps tend to produce smooth papers because of the plastic nature of the paper at the time of wet pressing.

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[133] Instrumentation Studies, *Paper Trade J. 106,* No. 4: 34–48 (Jan. 27, 1938)

[134] S. M. Chapman, *Pulp Paper Mag. Canada 48,* No. 3: 140–150, Convention Issue (1947)

Smoothness is related to the appearance of the paper because, as a general rule, a rough paper is unattractive. Paper with excessive wire and felt marks, or paper which is lumpy, fuzzy, or badly crushed is considered unsatisfactory. On the other hand, small even irregularities often give a pleasing appearance of pattern or texture. The most important factor is the average size of the surface irregularities, although the size, distribution, and arrangement of the irregularities are also important. Smoothness is of importance for writing papers where it affects the ease of travel of the pen over the surface of the paper. It is very important in printing papers because of its correlation with printing qualities, and the subject is discussed further in Chapter XIX. Smoothness is a factor in the pasting of papers.

Formation

Formation is defined as the uniformity with which the fibers are distributed in the paper. It is thus a physical property of the paper, although it is customarily measured by the degree of uniformity of light transmission through the paper.

Formation is often judged visually by looking through the sheet at a uniform light source. Naturally, the results of such an examination cannot be expressed numerically, and it becomes necessary to compare the specimen with a standard paper of acceptable formation or to rely on the judgment of the observer. Paper is said to have a uniform or close formation if the paper has a uniform texture similar to ground glass when viewed in transmitted light. The formation is said to be poor or wild if the fibers are unevenly distributed, giving the sheet a mottled or curdled appearance in transmitted light.

Formation is affected by the transparency of the paper since, in general, the more transparent the paper, the more readily poor formation shows up. For example, waxed paper generally appears more poorly formed than the same paper before waxing. The color of the paper is another factor, since blue papers generally appear wilder than white or yellow ones.

Formation can be measured by means of an instrument consisting of a photoelectric cell which scans the underneath side of the paper and a small beam of light of controlled intensity which is projected on the upper surface of the paper.[135, 136] The paper is moved at high velocity through the tester

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[135] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 103,* No. 27: 383–385 (Dec. 31, 1936)

[136] M. N. Davis, W. W. Roehr and H. E. Malmstrom, *Paper Trade J. 101,* No. 4: 43–48 (July 25, 1935)

so that the amplitude and frequency of variation in transmitted light can be measured on the photoelectric cell. Another suggested method of measuring formation is to cut small disks (0.25–0.50 in. diameter) out of the paper at regular intervals (or from obvious thick and thin spots) for weighing on a sensitive balance. This method is, of course, too laborious for routine testing.

Formation is of great importance because it not only affects the appearance of the paper, but also because it influences the physical and optical properties of the paper. Formation affects both the average value and the uniformity of values of nearly all physical and optical properties. Good formation is essential in writing and printing papers. Paper to be impregnated or coated should also have good formation. On the other hand, tissues and blotting papers do not necessarily require good formation.

Uniformity and Precision of Test Methods

Uniformity is a highly desirable characteristic in all papers. Uniformity in fiber distribution (formation) is necessary to obtain satisfactory appearance and good strength properties. Uniformity from top to bottom of the sheet (lack of two-sidedness) is desirable. Uniformity of properties from one edge of the sheet to the other, and from one lot of paper to the other, are essential requirements in high quality paper. Uniformity from lot to lot is particularly essential in the case of papers to be treated with substances which must be adapted to the paper, e.g., as in pigment coating, printing, impregnating, or laminating. If the paper in these operations does not run uniform from sheet to sheet or from roll to roll, considerable variation in results will be obtained in the converting operation.

Paper is never completely uniform. Different papers vary in uniformity, depending upon the grade of paper and care used in its manufacture. As a rule, heavy papers and papers made at slow speeds are more uniform than light papers and papers made on fast machines. The magnitude of the deviation of the arithmetical average obtained by a series of tests from the true value of the universe depends upon (*1*) the inherent non-uniformities in the sample as measured by the instrument, (*2*) the irregularities in the instrument, and (*3*) the number of readings taken. Statistics have been of great help in distinguishing between the uniformity of properties in different parts of the sample, the difference in properties between lots of the paper, and differences due to test method variability. The subject of statistics is discussed in Chapter XVII.

The physical tests commonly made on paper differ appreciably in precision, and hence the nature of the test must be taken into account in analyzing uniformity. Basis weight measurements, for example, usually run quite uniform on specimens taken from the same lot, since this test tends to average out small localized variations in weight. The basis weight of a given paper may thus run very uniform even when there is considerable variation in the formation or tensile strength. The method of measuring tearing resistance also tends to average out differences because several strips are torn at the same time. On the other hand, folding endurance generally shows wide variation because of the small area under test at any one time.

Some years ago, the Institute of Paper Chemistry[127] carried out a study of the magnitude of variation in the different properties of typical papers of standard grades and basis weights. Three different grades were used, bond, mimeograph, and ledger, so that the results are indicative of those obtained on fine papers. The probable error for each test (the error plus or minus from the true average within which a test result has an equal chance of falling) was calculated and then expressed as a percentage of the average reading. Probable error was calculated as:

$$\frac{8.85\Sigma(V)}{N\sqrt{N-1}}$$

The per cent probable errors for each grade were then averaged to give an average for each test based on the three grades of paper tested. The results, which are reported in Table XIII, indicate that maximum deviations occur in all tests, with the exception of thickness and basis weight.[127] It was concluded that deviations, in the main, are the result of lack of uniformity in

TABLE XIII

VARIABILITY OF PHYSICAL PROPERTIES OF PAPER

Paper property	Average per cent probable error
Opacity—Bausch & Lomb (contrast ratio)	0.291
Basis weight—Thwing basis weight scale (pounds 17 × 22—500)	0.566
Caliper—Schopper micrometer (inches/1,000)	0.587
Apparent density (basis weight/caliper)	0.602
Bursting strength—Perkins Mullen tester (pounds/square inch) (per cent points/pound)	1.612
Tear—Elmendorf tear tester (grams per 16 sheets)	2.03
Tear-across (grams/16 sheets)	2.65
Tensile strength—Schopper hand-driven model (pounds)	2.29
Tensile strength—across (pounds)	1.93
Stiffness—Gurley stiffness tester (milligrams)	2.69
Stiffness—across (milligrams)	4.37
Per cent stretch—Schopper hand-driven model	3.04
Per cent stretch—across	4.08
Porosity—Gurley densometer (seconds)	4.88
Folding endurance—Schopper (double folds)	6.08
Folding endurance—across (double folds)	8.20

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[127] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J.* 106, No. 3: 28-30 (Jan. 20, 1938)

properties, rather than lack of precision or accuracy in test methods. On the other hand, Reitz and Sillay[137a] found that the largest factor contributing to variance of results was inherent test method variability. They found that precision varied from ± 10% to ± 60% at the 3 sigma assurance level, depending upon the physical test under consideration and the paper upon which the test is run.

It is well known that the properties of paper vary with the basis weight. In order to compensate for this variation, it is common practice to divide the test result by the basis weight and report the result as strength factor or per cent points. This method of reporting tends to correct for small differences in results due to differences in weight, but the correlation appears to vary for different papers, and hence it is not valid in all cases.[137] This method of correction works fairly well for bursting strength, but seems to be entirely fallacious in the case of tearing strength, because tearing strength tends to increase at a proportionately greater rate than the increase in basis weight.

Unsatisfactory Appearance and Dirt

Unsatisfactory appearance is probably the greatest cause for the rejection of paper. The principal cause of unsatisfactory appearance is dirt, i.e., the presence of minute particles of foreign matter which seriously detract from the appearance and brightness of the paper. Dirt is particularly offensive in writing and printing papers and in the higher grades of wrapping papers.

Dirt may be defined as any foreign matter which is embedded in the sheet and has a marked contrasting color to the rest of the sheet (when viewed by reflected light), and which has an equivalent black area of 0.04 sq. mm. or more. The equivalent black area is defined as the area of a black spot on a white background which makes the same visual impression as the dirt speck has on the paper.[138] Light-colored spots on white paper or black spots on colored paper have a lower estimated equivalent black area than black spots of the same size on white paper. Thus, certain specks may have a low equivalent black area in unbleached pulp but a high equivalent black area in bleached pulp. Shives and spots which show up only at certain angles of observation are not considered as dirt.

Dirt is determined by counting the number of dirt specks in a given area of the paper and by estimating the equivalent black area of the specks. Standard comparison charts having a series of black spots (round and rectangular) of different areas on a white background are used for estimating the equivalent black area of each spot.[139] The test sheet is laid on a white

[137a] L. K. Reitz and F. J. Sillay, *Tappi 33*, No. 10: 504–506 (Oct., 1950)

[138] TAPPI Standards call for an equivalent black area of 0.04 sq.mm. or more for paper and 0.08 mm. or more for pulp.

[139] Charts may be obtained from the secretary of the Tech. Assoc. of the Pulp & Paper Ind., 122 East 42nd St., New York, N. Y.

background and illuminated with a 50-watt frosted bulb placed 4 ft. away. The standard chart should be held over the edge of the specimen and all specks graded by selecting a spot on the standard chart which is equally noticeable when both are held at a distance from the eye. Both sides of the sheet should be examined. Shives or spots which do not appear dark at all angles of observation should not be counted. The results are generally reported as the total equivalent area of dirt in square millimeters of equivalent black area per square meter of surface examined, i.e., as parts per million. In some cases, the results are reported as the number of particles per square foot of surface, but this is less satisfactory than the above method.

The method described above can also be used for measuring dirt count of pulp. A surface count is considered satisfactory on pulp since it has been found that the total area of visible dirt on the surface bears a close relationship to the total dirt in the whole pulp sheet.[140] A quick estimate of the amount of dirt in pulp samples can be obtained by comparing with standard samples of known dirt content.

The total dirt count depends upon (*1*) the type of light used for examining the paper (i.e., whether reflected or transmitted light), (*2*) the type of dirt specks, and (*3*) the frequency distribution.[141] Some specks are more readily observed by reflected than by transmitted light, and vice versa, but too much reflected light reduces the total number of specks observed because of glare and internal reflection. According to Graff,[142] the largest number of specks and the largest area of dirt per square meter is obtained when the sheet is examined with a single 20-watt daylight fluorescent lamp, using reflected light and a chinrest at 14 in. Frequency charts[142] which divide the dirt specks into classes according to size are more useful in summarizing the data and disclosing the type of dirt which is most objectionable than just reporting the total of all visible specks without regard to size. Graff[141] obtained the results in Table XIV for a mimeo bond. These results show that while the large specks are few in number, they constitute an appreciable percentage of the total dirt area. On the other hand, small specks constitute an appreciable part of the total number of specks, but an insignificant part of the total dirt area.

TABLE XIV

DIRT COUNT ON MIMEO BOND

Class	Area of speck, sq.mm.	Percentage by number	Percentage of area
Small specks	0.00–0.05	4.59	0.83
Medium specks	0.05–0.50	91.00	82.32
Large specks	0.50 and up	4.41	16.85

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[140] J. d'A. Clark, *Paper Trade J. 96,* No. 26: 27–28 (June 29, 1933)

[141] J. H. Graff, *Paper Trade J. 124,* No. 26: 292–298 (June 26, 1947)

Some causes of spots in paper are slime spots, colored fibers, color specks, shives from incomplete cooking or screening, undefibered waste paper, bits of string, dendrites, oil spots, foam spots, metallic particles, pieces of coal, bits of rubber, bark, alum, bleach scale, wood resins, and rosin spots. The methods of identifying dirt specks are described in the section on microscopical analysis of paper. Many spots are not counted in a dirt estimation because they are visible only at certain angles of illumination. The pulp supply is generally the greatest source of dirt. Graff[142] found in an analysis of standard mimeo bond that over 80% of the specks (both by number and weight) are due to resin specks.

It should be pointed out that there are many other causes of unsatisfactory appearance, aside from dirt. Some of these are as follows: too pronounced wire marks, marking caused by seams or bad spots in the wire, wrinkling or cockling of the sheet, crushing due to excessive pressure at the wet end, calender cuts, calender blackening, fish eyes, foam spots, slime spots, ragged edges, presence of shavings and paper dust, and grainy edges.

Two-Sidedness

Paper never has identical appearance and surface characteristics on both sides of the sheet. This difference in appearance of the two sides of paper is referred to as two-sidedness. All papers have a certain amount of two-sidedness in that the top side of the paper is smoother and has a closer formation than the wire side.

Two-sidedness may be an actual structural two-sidedness due to greater concentration of size, pigment, or fines on one side of the sheet, or it may be an optical two-sidedness caused by a difference in the finish or reflectance on the two sides of the sheet. Most papers, particularly thick papers, show definite two-sidedness in regard to fibrous composition. This is usually manifested in a preponderance of larger fibers on the wire side and a preponderance of finer, smaller fibers on the felt side. White papers sometimes show a higher brightness on the wire side than the top side, due to the greater removal of the dark-colored fines from the wire side.

Two-sidedness may be caused by one or more of the following factors: (*1*) loss of fine fibers through the wire before a mat of the larger fibers is laid down; (*2*) slower settling of the fine fibers, due to their reduced specific gravity and hydrodynamic resistance, with the result that a higher percentage of fines are deposited on the top side of the sheets; (*3*) removal of the finer fibers from the underside of the wet sheet after formation, due to the action of the table rolls and suction boxes. Increased machine speeds have increased the amount of two-sidedness. Smith[143] has shown that two-sidedness is not due to increased suction at the suction boxes, but instead is caused by a washing or flooding of the underside of the wet sheet each time the sheet passes over a table roll. Varying the amount of suction (in making hand sheets in the laboratory) showed that increased suction actually results in a preponderance of fines on the wire side, the opposite effect from that obtained on the paper machine.

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[142] J. H. Graff, *Paper Trade J. 124,* No. 26: 292–298 (June 26, 1947)

[143] J. F. Smith, *Paper Trade J. 129,* No. 21: 468–470 (Nov. 24, 1949)

The composition of the original pulp is a factor in the amount of fiber two-sidedness. As would be expected, paper made from pulp of uniform fiber length tends to show less two-sidedness than paper made from a pulp having a wide variation in fiber length. An examination of a typical bond paper showed about 18% fines on the felt side and about 11% fines on the wire side.[145] The effect of the greater concentration of fine material on the felt side is (*1*) to increase the bonding strength, (*2*) to increase the smoothness, and (*3*) to improve the writing and printing qualities of this side of the paper.

Colored two-sidedness exists where there is a greater depth of color on one side of the sheet. This condition may be due to a number of causes, but it generally occurs at the same time as structural two-sidedness because of the greater concentration of more highly dyed fiber fines on the felt side of the paper.[146] The subject of color two-sidedness is discussed at greater length in the chapter on coloring.

Paper is often two-sided in regard to sizing. Lee[147] was able to show, in the case of papers two-sided in sizing (as measured by the pen and ink test), that there is a difference in the amount of rosin on the two sides of the paper. The usual condition is for paper to show a good size test on the felt side and a lower test on the wire side, particularly if the rosin size has been precipitated in the form of relatively coarse particles and the paper made on fast machines (see Ch. X).

Nearly all pigment-filled papers have a higher concentration of pigment on the top or felt side of the paper, due to preferential removal of pigment from the wire side during formation (see Ch. IX). This results in an appreciable difference in color, brightness, or finish between the two sides of the sheet.

Two-sidedness is ordinarily undesirable, since it results in a difference in surface properties between the two sides of the sheet which affects the utility of the paper. In some cases, however, two-sidedness is intentionally sought after for reasons of economy or improved product. For example, paperboards made on a cylinder machine are often made intentionally two-sided by using different grades of stock in the liner and filler plys. In this way, cheaper stock can be used in the filler and more expensive stock used in the outside plys. The filling and sizing is often different in the various plys. Calender coloring of paperboard and the lamination of paper to one side of paperboard are other examples of a deliberate attempt to produce a "two-sided" product. In the case of certain Fourdrinier papers, a two-sided paper is intentionally produced by using a secondary head box[148] for applying stock to the top of the sheet on the paper machine wire at a point where the sheet is set on the wire side, but is still sufficiently wet on the top side to allow comingling of the fibers. In this way, a marked difference in the properties of the two sides of the sheet can be obtained.

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[145] O. Kress and E. J. Loutzenheiser, *Paper Trade J. 114,* No. 11: 133–136 (Mar. 12, 1942)

[146] E. R. Laughlin, *Paper Ind. 24,* No. 7: 709–711 (Oct., 1942)

[147] H. N. Lee, *Paper Trade J. 103,* No. 27: 386–390 (Dec. 31, 1936)

Dimensional Stability

The change occurring in the dimensions of paper with changes in the moisture content is an important consideration in the use of the paper. All papers expand with increasing moisture content and contract with decreasing moisture content, but the rate of change and the extent of change vary with different papers.

Dimensional changes are due to two factors: (*1*) the drawing together (or pulling apart) of the fibers and (*2*) the contraction (or swelling) of the individual fibers. Both are involved in ordinary dimensional change, but the movement of fibers in relation to one another is a more important factor than the expansion and contraction of the individual fibers. Much of the actual fiber movement is taken up internally in the paper, but some is transmitted into dimensional change. The amount involved in dimensional change is determined in large part by the way in which the sheet is formed, particularly by the amount of tension on the sheet during drying. Paper expands much more in the cross direction than in the machine direction, in part because of the greater expansiveness of the fibers in the cross direction and more importantly, because of the greater expansiveness built into the paper in the cross direction on the paper machine. The type of pulp used, degree of beating of the pulp, and the effect of fillers and starches are other factors influencing the expansiveness of paper.

Some of the grades of paper requiring a high degree of dimensional stability are printing papers, map papers, wallboards, machine-sorted classification cards, and recording papers. Because of the great importance of dimensional stability in printing papers (particularly offset), the subject is discussed at greater length in Chapter XIX. Aluminum-mounted papers are sometimes used in making map papers where expansion must be held to a minimum.

The amount of dimensional change can be measured by a suitable device which measures the length of the paper before and after conditioning to a definite moisture content. This can be done by clamping strips of paper (24 in. in length) between a fixed clamp and a loading clamp which applies a tension to the paper of 50 g. per inch of width. The change in length of the specimen during the period of the test can be measured by using a suitable magnifying device. The device is located in a cabinet equipped with a fan and a tray to which various salt solutions can be added for controlling the humidity.[149] In carrying out the test, the specimen is first conditioned at a relative humidity of 50% or lower, and then at 80% or above. The length is measured at the higher humidity, and the change in length is noted as the sample is conditioned at successively lower humidities down to a humidity of 50%. A curve can be plotted showing change in length versus relative humidity. The final result is reported as the percentage change of length on decreasing the relative humidity from 65 to 50%.

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[148] G. R. Tennent, *Paper Ind. 27,* No. 9: 1357–1358 (Dec., 1945)

Expansion and contraction of paper is greater for beaten than for unbeaten stock. It is greater for papers made from chemical pulp than for papers made from mechanical pulp.[150] On an equal strength basis, expansiveness is greater for papers made from wood pulp than for papers made from rag fibers, because more beating is required in the case of wood pulps to develop the desired strength. Expansiveness is reduced by the presence of clay or other fillers,[151] and by the presence of plasticizers.[152] The expansion which takes place when the relative humidity is changed from 25 to 65% is shown in Table XV for several different papers.[153] As can be seen from these results, the ratio of cross direction to machine direction expansion is always greater than 2 to 1. The rate of change of dimensions is de-

TABLE XV

EFFECT OF MOISTURE ON EXPANSION OF PAPER
Relative humidity changed from 25 to 65% at 25° C.

Type of paper	Per cent increase in extension		
	Cross direction	Machine direction	Ratio of cross to machine direction expansion
News	0.35	0.13	2.7
Tablet	0.38	0.12	3.16
M.F. Book	0.33	0.16	2.06
S.C. Book	0.47	0.10	4.7
Bond	0.31	0.13	2.3
Bond	0.48	0.10	4.57
Greaseproof	0.95	0.16	5.93

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[149] See TAPPI Standards

[150] S. F. Smith, *Paper-Maker 119*, No. 3: 185–192 (Mar., 1950)

[151] C. G. Weber, M. B. Shaw and M. J. O'Leary, *Paper Trade J. 117*, No. 13: 147–152 (Sept. 23, 1943)

[152] N. R. Pike, *Paper Trade J. 102*, No. 5: 63–66 (Jan. 30, 1936)

[153] G. Larocque, *Pulp Paper Mag. Canada 37*: 199–209 (Mar., 1936)

pendent upon the porosity of the paper. Porous papers (e.g., newsprint) change in dimensions more rapidly than non-porous papers (e.g., glassine).[153]

As mentioned above, the origin of paper expansiveness is in the strains built into the paper when the natural shrinkage of the paper is resisted during drying. A part of this dried-in strain is permanently recoverable by wetting and redrying the paper. If the wetting and drying cycle is repeated, further contraction takes place, although the per cent contraction decreases with each successive cycle. The results in Table XVI were obtained by Smith[154] on a sulfite paper. These changes are irreversible.

TABLE XVI

EFFECT OF WETTING AND DRYING ON CONTRACTION OF PAPER

Wetting and drying cycle	Per cent contraction
1	1.80
2	0.55
3	0.30
4	0.16

Irreversible changes in dimensions also occur when paper is subjected to high humidity, i.e., 90% or above, for a period of time. The amount of contraction obtained on four different papers which were measured at 50% R.H., conditioned at 90% R.H., and then remeasured again at 50% R.H. is shown in Table XVII.[155] These results show that the dimensions of paper on desorption of moisture are smaller than those obtained on absorption of moisture, in spite of the fact that the moisture content of the paper is higher in the former case. This reduced expansion in the face of higher moisture content is attributed to the gradual release of strains in the paper at high humidities. Results obtained by Larocque[155] on several different papers

TABLE XVII

EFFECT OF HIGH HUMIDITY ON CONTRACTION OF PAPER
Per cent contraction which takes place at 50% R.H.
when paper is subjected to 90% R.H.

Paper	Cross direction	Machine direction
News	0.15	0.09
Bond	0.07	0.20
S.C. Book	0.17	0.08
Offset	0.12	0.08

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[154] S. F. Smith, *Paper-Maker 119,* No. 3: 185–192 (Mar., 1950)
[155] G. Larocque, *Pulp Paper Mag. Canada 37:* 199–209 (Mar., 1936)

are shown in Figure XVI-18 where it can be seen that the various papers were extended less on desorption than on absorption for a given moisture content. This effect was noticeable in both the machine and cross directions of the bond and greaseproof papers, but only in the machine direction of the newsprint. Once the strains are released by subjecting the paper to a high humidity, subsequent expansions and contractions take place in a more reversible and reproductive manner.

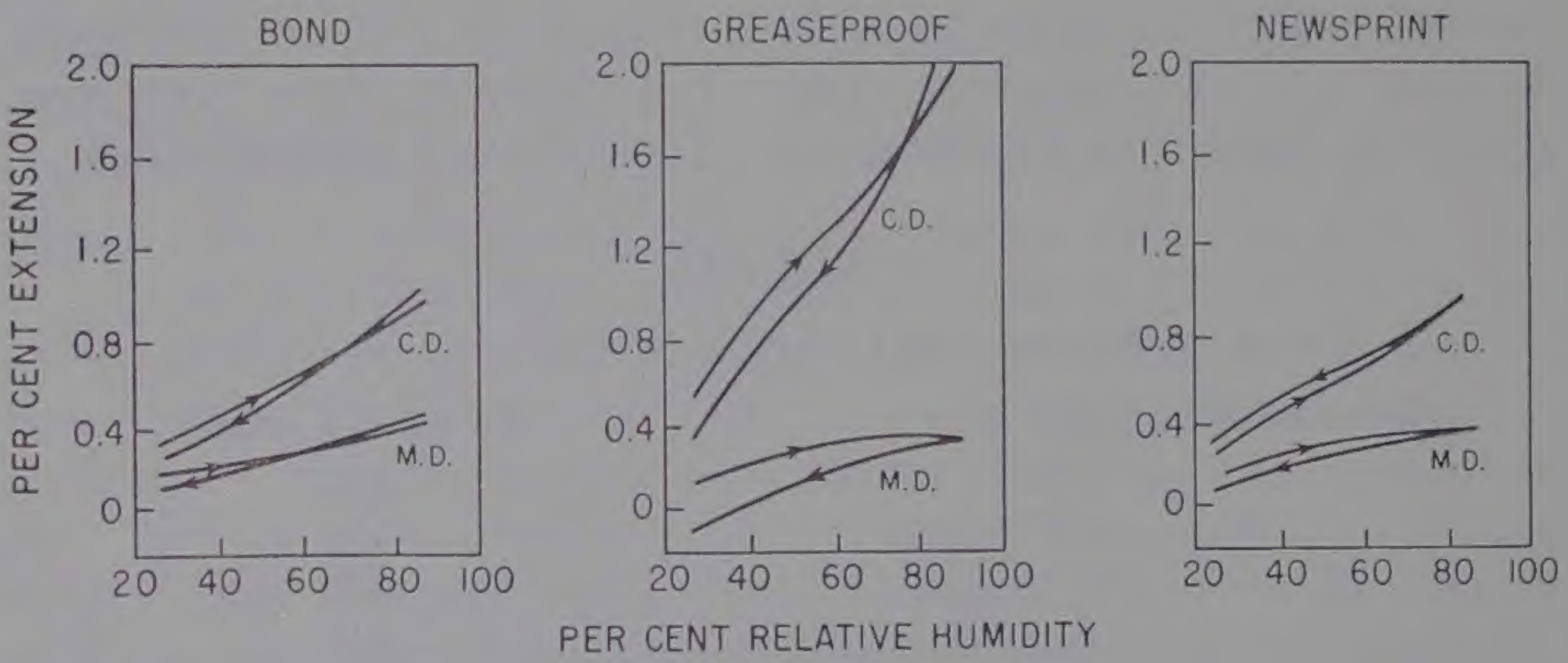

Fig. XVI-18. Effect of relative humidity on per cent expansion of paper for absorption and desorption of moisture.

Curl is a problem closely related to dimensional change. Curl is affected by the dimensional stability, uniformity of the paper, thickness of the paper, and amount of two-sidedness. There are several forms of curl: curl to the wire side of the sheet, curl to the felt side, and curl partly to the wire side and partly to the felt side. Curl is caused by uneven expansion or contraction of the paper.

Curl is more pronounced with thin papers than with thick papers, because thin papers have less physical resistance to curl. Papers made from long, highly beaten fibers are more likely to curl than papers made from short, free fibers, because greater tensions and unrelieved stresses are set up in the former case. The softer and more flexible the paper, the less its tendency toward curl. A dense paper will curl under conditions where a soft, porous paper will remain practically flat. Moist papers tend to curl proportionately less than papers which are very dry. Loading, as a rule, decreases curl, since it reduces the overall cohesiveness of the paper. Rosin-sized papers seem to curl more than unsized papers. Other conditions causing curl are faulty machine conditions, such as dirty felts or poorly ground press rolls. Mechanical breaking of the paper as a result of sharp bending may disrupt the fibers or break the surface layer and produce curl.

In general, four types of curl are recognized: (*1*) inherent curl, which is built into the paper and shows up immediately; (*2*) delayed curl, which is roughly the same as inherent curl, but shows up on aging; (*3*) structural curl, which is caused by physical differences in the two surfaces of the paper; (*4*) moisture curl, which is the result of dimensional change caused by changes in the moisture content.

Inherent, delayed, and structural curl are caused by much the same factors. These factors involve conditions which result in two-sidedness or in some way create a built-in strain in the paper. Inherent curl is almost impossible to correct. It is due to uneven drying or finishing, uneven rosin or surface sizing, uneven loading, or by the natural difference in cohesiveness between the wire and felt sides of the paper. The most common type of inherent curl is curl of the grain edge toward the wire side with axis of the curl parallel to the machine direction.[155a] This is caused by uneven stress on the two sides of the sheet which is later released upon sheeting. Another less frequent type of inherent curl is curl of the cross grain edges toward the wire side. This is caused by tensions built into the sheet in the machine direction, and since the wire side has the more pronounced grain, the contraction is greater on that side when the tensions are released.[155a]

Water-finished or calender-sized paperboard, upon removal from the paper machine, tends to curl toward the side which received the most moisture in the sizing operation. Hence, moisture addition in calender sizing must be controlled by regulating the number of water boxes used or by controlling the degree of sizing in the top and bottom surfaces of the board. Curl can be controlled in the drying operation by regulation of the steam to the various drier rolls. For example, if the underside of the paperboard is being dried more than the top side (due to the admission of more steam to the upper row of driers), built-in strain results on the underside. This arises from the fact that the underside of the paper is not free to contract, due to the tension on the paper, whereas the top side, when it dries out later to the same moisture content, is under no tension and can freely contract, with the result that the sheet curls toward the upper side.[156] As evidence that surface contraction is the cause of curl, Smith has shown, in the case of paperboard, that the measured shrinkage of the top liner (which was detached from the rest of the board by inserting tissue paper between the first and second plies on the machine) is the same upon wetting as the shrinkage calculated from the curl by use of the following formula:

$$s = 100t/\gamma$$

where, s is the percentage contraction of the liner, t the thickness of the board, and γ the radius of curl.

[155a] A. E. Erspamer and W. D. Rice, *Paper Mill News 73,* No. 28: 76–78, 88 (July 15, 1950)

[156] S. F. Smith, *Paper-Maker 119,* No. 3: 185–192 (Mar., 1950)

Paper sometimes takes on a permanent curl after it has been subjected to tension for a long period of time. This is caused by a phenomenon referred to as micellar creep which causes an expansion in the outside layer of the sheet. This phenomenon occurs when paper is stored in roll form, and is more pronounced in the inner part of the roll. Reel curl is an example of this type of curl.

Moisture curl is related to the dimensional stability of the paper. Paper exhibits moisture curl when the two sides of the sheet expand or contract unequally on account of uneven absorption of moisture. Wrinkling and wavy edges result from the localized absorption of moisture which sets up localized strains in the paper. This freqeuntly occurs when paper is piled in a moist atmosphere or is moved from a cold warehouse into a warm room. Even if paper is exposed to the same atmospheric conditions on both sides, uneven expansion may result because of differences in the sizing, coating, or amount of finish on the two sides of the paper. In this way, moisture curl is related to structural curl. As a rule, hard-sized papers are more susceptible to moisture curl than soft-sized papers because they absorb moisture more slowly and take longer for the internal forces to equalize themselves. In general, the wire side of paper has greater expansiveness than the felt side, and consequently nearly all papers curl toward the felt side if too moist and toward the wire side if too dry. The axis of the curl is always parallel to the machine direction of the paper, except in the case of papers showing excessive reel curl or in some forms of inherent curl.

Paper wetted on only one surface, as, for example, paper coated with pigment on only one side, tends to curl toward that surface on drying. Curl, in this case, can be attributed to the release of built-in strain on the side of the paper which is wetted, thereby resulting in a disproportionate contraction of that surface upon drying. In the case of pigment-coated papers, the water in the coating mixture is responsible for most of the curl, but part of the curl can be attributed to the shrinkage of the adhesive on drying of the coating.[156]

Even if one-side pigment-coated paper is flat after coating, trouble with curl frequently occurs at high humidities. Curl, in this case, is caused by the differences in the hygroscopicity and in the coefficients of expansion and contraction between the fibrous surface and the coated surface, that is, the layer of coating is physically more uniform and tends to change more or less equally in all directions, whereas the uncoated surface undergoes a greater change of dimensions in the cross direction than in the machine direction. A coated one-side paper may, under some circumstances, curl less than an uncoated paper if the coating counteracts the greater expansiveness of one side of a normally two-sided sheet. The hardness of the coating and the amount of coating on the paper affect the amount of curl. Coated two-side paper generally curls less than uncoated or coated one-side paper because of the even expansion which occurs on both sides of the paper.

Curl is a problem in the developing of photosensitive papers (diazotype papers), pasting of paper, printing of paper, and, as mentioned above, in the coating of paper. Curl is a frequent cause for complaint with carbon papers. Gummed papers are also highly susceptible to curl, the curl taking place toward the gummed side if the moisture is too low and to the ungummed side if the moisture is too high. Plasticizers in the glue line help the situation somewhat. In the case of certain label papers, curl is desirable and is sometimes intentionally imparted to the paper in supercalendering to produce a curl toward the side of the label going against the bottle. The subject of curl is discussed further in the chapters on laminating and printing.

The maximum curl of paper can be measured in the Carson curl tester by allowing a specimen of the paper to fall across a definite area of water and then measuring the maximum angle through which the sheet curls.[157] The result is reported as the maximum curvature in degrees per centimeter of arc. The results are obtained by adding the average of the readings to the fixed angle of 30°, which the other end of the specimen makes with the horizontal, and dividing by the length of arc of the wetted, curled part of the specimen in centimeters. The result is an indication of the tendency of the paper to curl.

Cockling (localized buckling of paper) is due to local expansion or contraction of the paper. Cockling can be attributed to local variations in basis weight, moisture content, density or other properties of the paper upon leaving the paper machine which result in local built-in strains in the paper.

Optical Properties

The optical properties of paper are as important, or more important, than the physical properties of paper. Some of the grades of paper where optical properties are of primary importance are printing papers, transparent wrappings, and writing papers. An understanding of the optical properties is necessary to understand such important paper properties as opacity, transparency, brightness, gloss, and color.

The optical properties of paper are determined by the relative amount of light reaching the paper and the manner in which the incident light is reflected, transmitted, and absorbed by the paper. The optical properties are affected by the optical properties of the materials in the paper. Some of the important factors are: (*1*) degree of whiteness of the pulp, (*2*) presence of white pigments (fillers or surface coatings), (*3*) presence of dyestuffs or colored pigments, (*4*) method of stock preparation and sheet formation, and (*5*) presence of minor ingredients (e.g., rosin and starch).

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[157] See TAPPI Standards

Nature of Light

It was established years ago that white light is composed of a spectrum of radiations of electromagnetic waves of wavelength between 400 to 700 millimicrons, each wavelength or wavelength range being associated with a different color or hue. When the wavelength range is very small (e.g., 1–2 millimicrons), the light is known as monochromatic light. Monochromatic colors can be represented, roughly speaking, by the following wavelengths (millimicrons):

Violet	400–450
Blue	450–500
Green	500–570
Yellow	570–590
Orange	590–610
Red	610–700

These are only approximate values, since colors vary from wavelength to wavelength. Radiation smaller in wavelength than 400 millimicrons is called ultraviolet light, whereas radiation greater in wavelength than 700 millimicrons is called infrared; both of these are invisible to the human eye.

Before undertaking a discussion of the optics of paper, it is necessary to define certain of the terms used in connection with light measurements. A few definitions are given below:

The *candlepower* is the unit of luminous intensity of the light source.

Luminous flux is the time rate at which radiant energy is transmitted.

Illumination is the density of luminous flux per unit of area, i.e., the quantity of light that falls per second upon a unit area of illuminated surface.

Brightness refers to the light reflected from the surface; it may be expressed in terms of flux or in terms of intensity.

The *reflectivity* is the ratio of the light reflected from a surface to the light incident upon it.

Absorption of Light

Absorption of light refers to the capacity of paper for converting light energy into other forms of energy, usually thermal. Since all the light falling on paper is either reflected, transmitted, or absorbed, the amount of light absorbed can be measured indirectly by subtracting the sum of the reflected and transmitted light from the amount of incident light. The absorption coefficient, which measures the degree of conversion of light energy into other forms of energy, is influenced by the chemical nature of the sheet constituents (lignin content, dyestuffs, pigments, etc.), and to a lesser extent, by the degree of bonding and index of refraction of the sheet. Forni[158] obtained a straight-line relation between the specific absorption coefficient and the lignin content of paper up to about 1.85% lignin. The presence of dyestuffs in the sheet usually results in a selective absorption of light.

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[158] P. A. Forni, *Paper Trade J. 119,* No. 11: 108–112 (Sept. 14, 1944)

Reflectance of Light

When light strikes a smooth, optically flat surface, a high percentage of the incident light is reflected at an angle equal to the angle of incidence of the light so that the parallel rays of light are still parallel after reflection. This is known as mirror or regular reflection. It is possible, by using certain formulas, to compute the fraction of the incident light which will be regularly reflected at a given angle from an optically flat surface, if the refractive index is known.[159] Highly finished papers exhibit some regular reflection, although the amount of regular reflection is considerably less than that exhibited by highly polished glass or metal surfaces.

Regular reflection always takes place from the uppermost part of the surface. In the case of a perfectly matt surface, the light penetrates beyond the surface into the body of the material where the light is scattered approximately equally in all directions so that it emerges as a semicircle of diffused light. The amount of this diffused light depends upon the angle of incidence and the index of refraction of the material. Most of the light reflected from a paper surface is diffused light. In the case of glossy papers, the distribution of regularly reflected light about the angle of regular reflection is represented by a hump in the reflection distribution curve.[160]

Reflecting-measuring instruments are of two types: (*1*) those which measure specular (regular) reflection (glossmeters), and (*2*) those which measure diffuse reflection (brightness meters, opacimeters, and spectrophotometers). The sum of the specular reflectance and the diffuse reflectance makes up the total reflectance. Color or brightness readings must be evaluated on the diffuse reflection, care being taken to eliminate the glare of specular reflection, since it is only the diffuse light which penetrates into the surface of the paper far enough to define the color.

It is customary, when making reflectance measurements, to denote the reflectance of the paper when backed by the appropriate body. The body used for backing is denoted by the use of subscripts. Reflectance (R) may be reported in any one of the following ways:

(*1*) R_0, which is the reflectance when a single sheet is backed by a black cavity.

(*2*) R_∞, which is the reflectance of a pad of the test paper thick enough so that no change in reflectance occurs when the backing is doubled. (When this reading is made at a wavelength of 457 millimicrons, it is known as papermaker's brightness.) This is an intrinsic characteristic of paper.

(*3*) $R_{R'}$, which is the reflectance of a single sheet when backed with a standard white body having an absolute reflectance of R'.

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[159] R. S. Hunter, "The Glossmeter," Science Section Circular, 456, National Paint, Varnish and Lacquer Association, Washington, D. C. (1934)

[160] R. S. Hunter, *Paper Trade J. 100,* No. 26: 335–337 (June 27, 1935)

All reflectance values given the designation *R* should be absolute values based upon values obtained on a primary standard. A primary standard can be prepared by depositing a thin film (0.5 mm. or more in thickness) of magnesium oxide on the surface of a suitable base material by exposing the base material to fumes of burning magnesium. Magnesium oxide prepared in this way has a highly diffusing surface and a total light reflectance of about 97 to 98%; the reflectance varies less than 1% with wavelength. The oxide is fairly stable, although it tends to become slightly yellow with time, resulting in a decrease in the reflectance of the light of wavelength less than 550 millimicrons. A block of magnesium carbonate can also be used as the primary standard if it is freshly prepared by scraping. It has a reflectance of 97.5% in the red and green, and a reflectance of 96.5% in the blue.

In reporting results in absolute reflectance, it is necessary to multiply reflectance readings based upon magnesium oxide as the standard by the absolute reflectance of magnesium oxide, i.e., 0.97. Thus, assuming that the reflectance of a paper sample was found to be 85% relative to magnesium oxide as 100%, the absolute reflectance of the paper can be obtained by multiplying 0.85 by 0.97, the absolute reflectance of magnesium oxide. For regular routine testing, secondary working standards calibrated to an absolute reflectance based on freshly prepared magnesium oxide are generally used. These may be enameled iron, opaque glass, or glazed tiles. Reflectance readings made on an absolute basis can be related mathematically by using simple calculations, as will be shown later.

Color of Paper

One of the most important optical properties of paper is the color of of paper. Color has already been discussed from the standpoint of the coloring process, but the properties of colored paper are discussed in the following sections.

A perfectly white or a perfectly gray body reflects light of all wavelengths to the same degree. A colored (opaque) body preferentially reflects light in one or more of the wavelength ranges, due to greater absorption of light in the other wavelength ranges. For example, paper colored with methyl violet shows preferential absorption of light in the wavelength range between 550 to 600 millimicrons, which is the yellow part of the spectrum.

It should be emphasized that every dyestuff and pigment acts by absorbing light, never by increasing the amount of reflection. Exceptions are the very bright white pigments (e.g., titanium dioxide) which are brighter than the paper, and certain dyestuffs (called white bleaches or white dyes) which absorb practically no visible light, but do absorb ultraviolet light which is re-emitted as visible light. In general, however, the stronger the color, the greater is the dulling effect. The amount of dulling resulting from the use of a particular dye depends upon the amount of light which the dye absorbs over the entire spectrum (see Fig. XVI-21).

No dyestuff is absolutely specific in absorption; even the brightest blues, which are probably the most specific, absorb some blue light and reflect some red and green light. Most bright red and yellow dyestuffs absorb light in the blue and green end of the spectrum without appreciably reducing the reflection of red light. As a result, they usually produce brighter sheets than green dyestuffs, which strongly absorb red and blue light, and also an appreciable amount of the green light.

Methods of Measuring Color. Color may be measured by psychological, physical, or by psychophysical means.[161] Psychological properties deal with the visual impressions of the observer. Physical properties are measured with optical instruments such as the recording spectrophotometer. Psychophysical properties are measured physically, but interpreted psychologically, using tristimulus values.

Color belongs to the realm of the psychologist, as well as to the realm of the physicist and chemist. Godlove and Laughlin[162] illustrate the difference in interpretation between the psychologist and the physicist by the use of a sample of gray paper which, psychologically speaking, appears to be halfway between a white (which reflects 100% of light) and a black (which reflects no light), but when examined by the instruments of the physicist, is found to reflect only 18% of the light.

Color is not a property of paper; it depends upon the following factors: the spectral characteristics of the illuminant, the geometrical conditions of illuminating and viewing, the spectral reflectance of the specimen, and the characteristics of the observer's eyes. The only color characteristic which is the same under all circumstances is the spectral reflectance of the specimen.

The reflectance of light from a sample of paper is a function of the scattering and absorption characteristics of the paper, the thickness of the paper, and the reflecting characteristics of the background. There is a minimum thickness required to obtain the true color of paper. The reason for this is that there must be ample opportunity for light to penetrate the paper in order for absorption to take place. Since the relative reflectivity of light of different wavelengths depends upon the thickness of the sheet, the resultant color depends to some extent upon the thickness of the paper. Lewis[163] points out that unfilled papers of both high and low opacity must be about 0.2 to 0.8 mm. in thickness (about 10–40 fiber diameters) to produce 99% of the true reflectivity. Coated papers have their final color at from 0.15 to 0.20 mm., whereas papers loaded with pigment develop their full color at a still lower thickness.

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[161] R. S. Hunter, "Photoelectric Tristimulus Colorimetry with Three Filters," U. S. Dept. Commerce, Natl. Bur. Standards, C429 (July 30, 1942)

[162] I. H. Godlove and E. R. Laughlin, *Paper Trade J. 111,* No. 17: 216–223 (Oct. 24, 1940)

[163] L. C. Lewis, *Paper Trade J. 103,* No. 22: 323–330 (Nov. 26, 1936)

Increased beating appreciably increases the depth of shade or color intensity, because it decreases the number of air-fiber interfaces at which reflection takes place, thus increasing the opportunity for increased absorption of light by the dyed fibers. Calendering increases the depth of shade by about 10 to 15% for the same reason.

Measurement of Color by Eye. Color may be defined as the psychological sensation produced in the brain of the observer by the action of visible light on the retina of the eye. The interpretation is different for each observer, since some people are more sensitive to color than others and, in fact, a few are totally color blind. The results of color matching are influenced by the mood and health of the observer, although most people are in fairly good agreement about the matching of colors. A trained observer can distinguish minute variations in shade which are difficult to measure with the finest optical instruments.

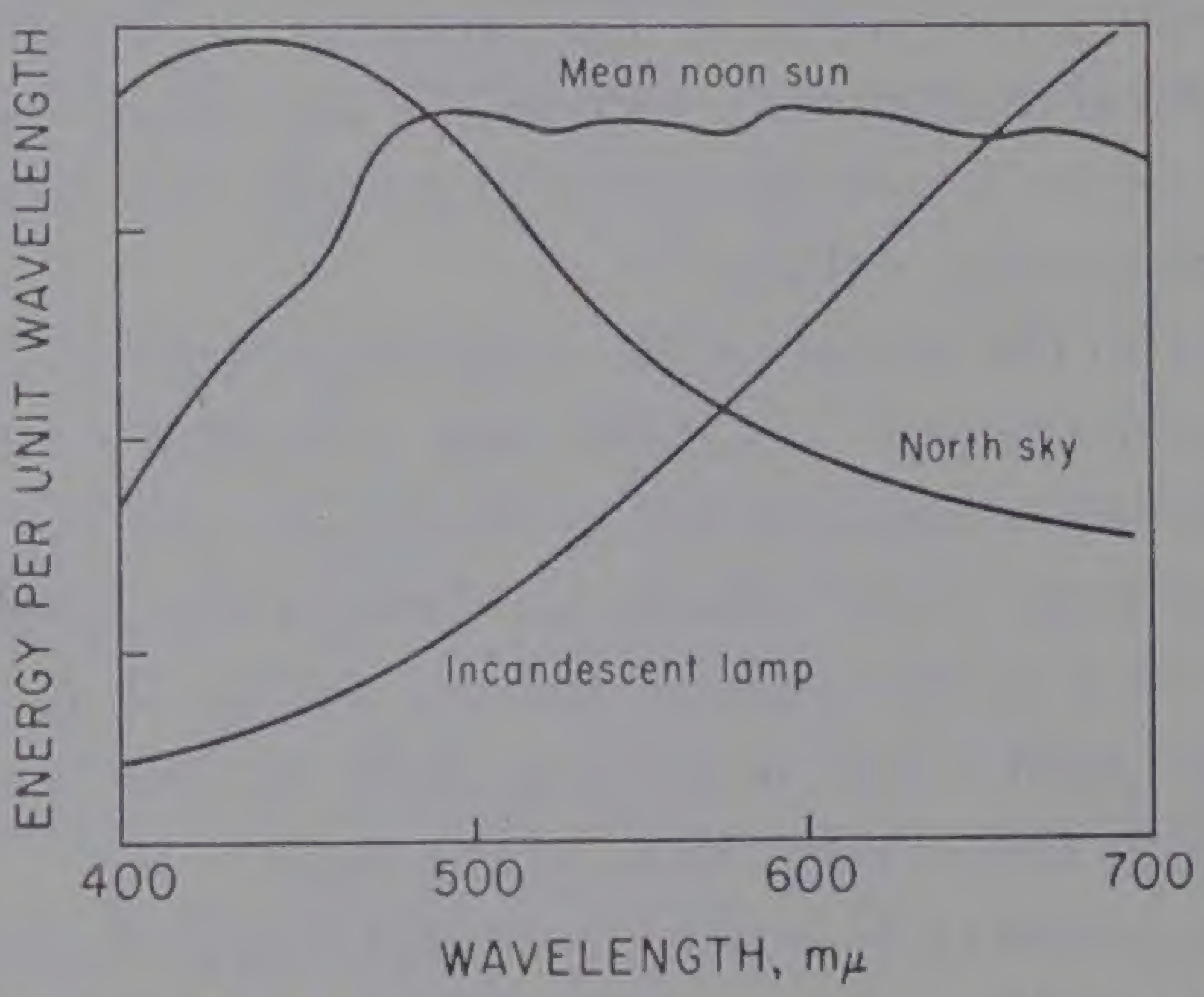

Fig. XVI-19. Comparison of three illuminants for energy per unit of wavelength.

Color depends as much on the spectral energy distribution of the illuminant as on the reflecting characteristics of the paper. Ordinary incandescent lamps have a high percentage of yellow light, but are deficient in blue light. The principal illuminants used for viewing paper are north sky light and special fluorescent (daylight) lamps. The ideal illuminant would be one having equal brightness at all wavelengths, but such an illuminant is not available. Comparison of three common illuminants is shown in Figure XVI-19.[163a] Sunlight has a nearly uniform distribution of energy throughout the spectrum. North sky light, on the other hand, has high brightness in the violet end of the spectrum and low brightness in the red end. The importance of the illuminating light can be illustrated by examining a green paper under ordinary white light and under red light. The sheet will appear green in ordinary light because it absorbs more red and blue light than green, but the same sheet will appear red when illuminated by monochromatic red light because it reflects a part of the red light. For the reasons given above, the color of paper is generally slightly different when examined in daylight than it is when examined under artificial light. For example, a certain paper may appear purple in daylight, appear almost red under tungsten light, and almost violet under north sky light.

[163a] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J.* **105**, No. 18: 285–291; No. 19: 293–306 (Oct. 28, Nov. 4, 1937)

The color sensation measured by the eye depends upon the energy distribution of the light entering the eye. The spectral energy distribution of light reflected from a colored body is determined by multiplying the amount of energy present in the light source at each wavelength by the fraction of the incident light reflected at the corresponding wavelength. The eye is not capable of analyzing for energy distribution; for example, the eye does not distinguish between a monochromatic red and a red composed of heterogeneous light.

The eye is very sensitive to small differences in hue (wavelength), but is less sensitive to depth or strength of color. Accuracy in estimating strength varies with the color, being least in the yellow and greatest in the red and blue range, but is generally considered to be about 5%.[164] The sensitivity of the eye to wavelength is greatest in the yellow-green range and decreases to practically nothing in the violet and red range. In other words, for the same intensity of radiant flux, that is, same amount of energy radiated per unit of area, a yellow light will produce much more illumination (luminous flux) than a red or a blue light. Thus, dyestuffs which show great differences in reflection in the extreme violet or red range have very little visual effect on the eye. The relation between luminosity (visibility) and wavelength is shown in Figure XVI-20, which is the accepted curve for the spectral sensitivity of the average human eye. The eye is particularly valuable in judging two samples differing only slightly in shade and strength, and since this is the case in most commercial color matching, visual color matching is generally quite effective.

In visual grading, glare should be avoided by viewing the specimen at an angle of 45° to the incident light; if the light falls on the sheet at 45° to the normal, the sheet should be viewed on the normal, and vice versa.

Expressing Color in the Munsell System. There have been many attempts to express color in terms which can be understood by anyone. One of the most used systems of specifying color subjectively is the Munsell system, which specifies three properties of color, hue, value, and chroma.

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[164] G. G. Taylor, *Paper-Maker 118,* No. 2: 99–105 (Aug., 1949)

Hue is determined by the dominant wavelength of the light reflected from the paper; it is represented in the Munsell system as an angle on a vertical plane. Value measures the total amount of light reflected to the eye; it is represented in the Munsell system by the distance above the horizontal plane which varies from black on the bottom plane to white on the top plane. Chroma measures the per cent departure from a neutral gray of the same value; it is represented by the distance from the vertical axis which varies from neutral gray at the center to the pure colors at the extreme distance from the axis.

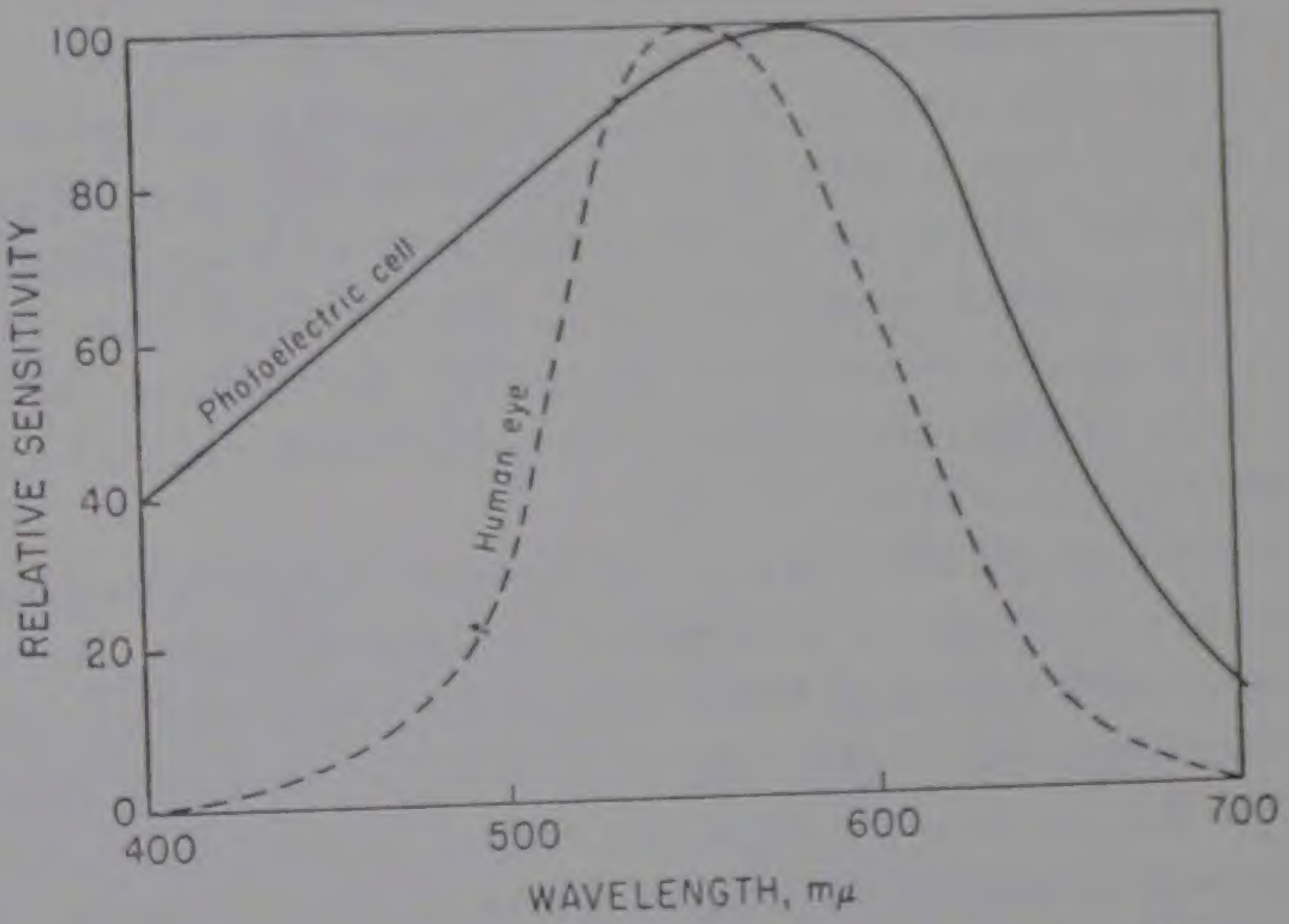

Fig. XVI-20. Sensitivity of human eye and photocell to different wavelengths of light for equal intensities of radiant flux.

The chromaticity of paper is specified by hue and chroma, and the color is specified by chromaticity and value. Observers sometimes tend to mistake hue and value, and this is often responsible for the difficulty commonly experienced in the visual grading of white papers.

Physical Measurement of Color. So far, color has been described principally from the standpoint of visual or subjective measurement. It is also possible to define color from the purely physical standpoint in terms of reflectance compared to some standard, when both the standard and the unknown are illuminated with a specific luminant and viewed under specific conditions. In the system developed by the International Commission on Illumination (I.C.I. System), magnesium oxide is used as the standard and is arbitrarily given the value of 100. Instruments for measuring color may differ in three respects, method of illumination, geometry of illuminating and viewing, and photometry.

In regard to spectral features, the light may be either monochromatic, approximately monochromatic, or non-monochromatic. Monochromatic light is preferred for all optical studies on paper and is absolutely essential for exact analysis of colored papers, although white light is sufficiently accurate in some cases for measuring the reflectance of white, near-white, or gray papers. Scattering of light is inversely proportional to the fourth power of the wavelength of the illuminating light, and reflection of light is directly proportional to the square of the wavelength of the illuminating light.[165, 166]

In regard to geometry, the following systems may be used:[167] (*1*) illuminating with a parallel beam at 45° and viewing on the normal; (*2*) illuminating with a parallel beam on the normal and viewing at 45°; (*3*) illuminating with an approximately parallel beam on the normal and measuring a quantity proportional to the integral of the angular distribution of the intensity of reflected light over all angles except those excluded by the apertures of the sphere; (*4*) illuminating with diffuse light and viewing an approximately parallel beam reflected normally at the surface. The color of paper relative to that of the standard surface varies markedly with changes in the illuminating and viewing angles, and hence these angles must be carefully specified. The illumination upon a surface inclined to the direction of the light rays is less than it would be if the surface were perpendicular to the light rays. Illumination is directly proportional to the cosine of the angle which the incident ray makes with the normal, and the brightness (luminous intensity) of emitted light is proportional to the cosine of the angle between the direction of the reflected ray and the normal. Glossy surfaces do not, of course, follow these laws. Illumination at 45° and normal viewing are specified for reflectance measurements in the International Commission on Illumination System. The distance between the light source and the object is important, since the intensity of illumination varies inversely as the square of this distance.

Photocells are used in optical instruments for measuring spectral response. Photocells produce a measurable photoelectric current which depends on the illumination or radiant flux incident upon the photocell surface and the spectral response of the cell. The spectral sensitivity of a photoelectric cell is shown in Figure XVI-20 in comparison with the human eye.[168] It can be seen from this figure that the cell is more sensitive than the eye in the blue and red regions, although filters can be used to make the spectral sensitivity more closely approximate that of the eye. There are two principal methods used with photocells for measuring the intensity of

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[165] A. W. Thomas, *Colloid Chemistry*, McGraw-Hill Book Co., New York, N. Y. (1934)

[166] D. H. Clewel, *J. Optical Soc. America 31:* 521–527 (1941)

[167] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 105,* No. 18: 285–291; No. 19: 293–306 (Oct. 28, Nov. 4, 1937)

[168] These curves were taken from bulletin, "Technical Data," Western Photronic Cell, Western Electrical Instrument Corp., Newark, N. Y.

light reflected from the sample and from the standard, the direct reading method and the null method. The direct reading method is based on a direct reading of the photocurrent produced by the cell on the assumption that this photoelectric current is directly proportional to the reflected light flux. This relationship is not completely valid, however, which makes it desirable to use calibration curves for the particular instrument set-up when this type of arrangement is used. The null method is based on the balancing of two photocurrents by varying the amount of incident or reflected light flux to compensate for differences in reflectance of sample and standard. A number of devices can be used to control the amount of light flux incident upon the photocell, e.g., iris diaphragm, sector diaphragm, polarization, neutral wedge, or wire screens.[169] The null method is more accurate than the direct reading method, since it compensates for variations in the photoelectric cell and light source. It is used in the Hardy recording spectrophotometer, General Electric photometer, and Hunter multipurpose reflectometer.

The Recording Spectrophotometer. Instruments called spectrophotometers are available for measuring reflectance as a function of wavelength. Curves, called color curves or spectrophotometric curves, can be prepared from data obtained on these instruments showing the percentage of light reflected for a given wavelength relative to the percentage reflected from a standard white surface (e.g., magnesium oxide or magnesium carbonate) at that wavelength under identical conditions of illumination and viewing. Spectral reflectivity curves for several deeply dyed papers are shown in Figure XVI-21.[170]

Spectrophotometric curves offer a means of measuring the true spectral properties of paper which can be kept as a permanent record. A minimum in the spectrophotometric curve represents an absorption band which is characteristic of the sample. The depth of the minimum indicates the proportion of material causing the absorption. The spectrophotometer offers a means of comparing one colored paper with another, and of obtaining an idea of what may be done in making two colors more alike. The instrument is particularly useful in making color measurements on standard orders of paper which must be kept constant in shade over a long period of time, and for checking the amount of fading of colored papers.

Two samples of colored paper may appear to match, even though their spectrophotometric curves are not identical. In this case, however, the two colored specimens are different physically, and while they may appear to match under a specific illuminant, they will not match under all illuminants. A color match can be made as long as the color curve of the sample in question is above that of the sample to be matched, but a match cannot be made, once the color curve falls much below that of the sample to be matched. It is difficult to obtain a color match from spectral reflectance data alone, but the complete color specification of the specimen can be calculated from spectrophotometric data, as will be shown later.

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[169] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 105*, No. 18: 285–291; No. 19: 293–306 (Oct. 28, Nov. 4, 1937)

[170] J. A. Van den Akker, J. E. Todd, P. Nolan and W. A. Wink, *J. Optical Soc. America 37*, No. 5: 363–387 (May, 1947)

The principal recording spectrophotometer is the Hardy, made by General Electric. In the Hardy spectrophotometer, a prism is used to disperse the light from a standard light source into a band of different wavelengths, and then a narrow slit is used to separate the light into very narrow bands, the width of the band for each color being about 10 millimicrons.

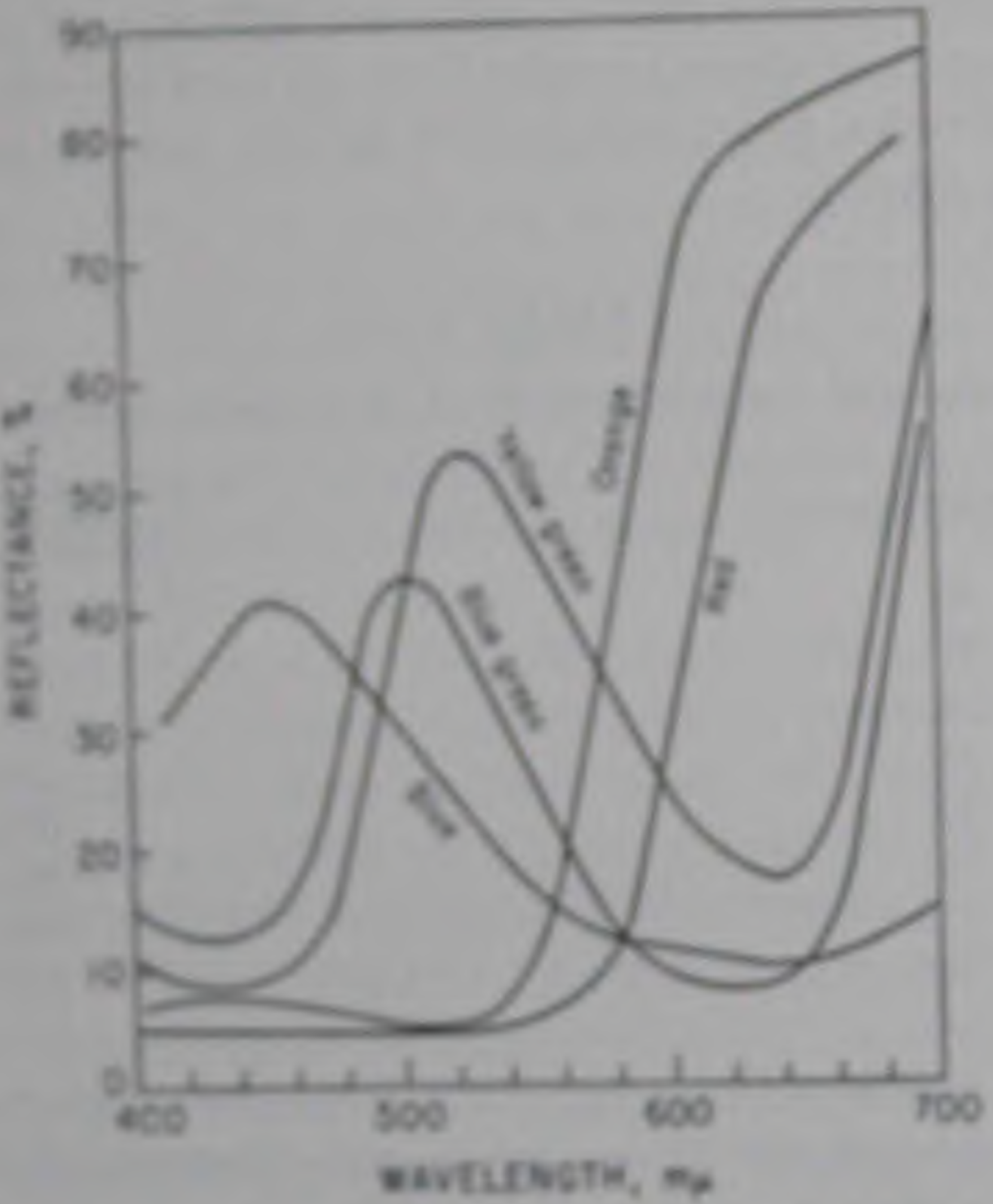

Fig. XVI-21. Spectral reflectivity curves for several deeply dyed papers.

The light is purified by passing it through a second prism and is then broken into two beams (variable in brightness and out of phase with each other). One of the beams is cast upon the specimen and the other upon a standard white surface, and both are collected in a white integrating sphere on a photocell. The two surfaces do not reflect the same amount of light so that the photocell puts out an alternating current. This current runs a small motor which controls the optical system so as to equalize the strength of the two reflected beams. The movement of the optical system controls a recording pen which plots the per cent reflection of light against wavelength. The optical system consists of a Wollaston prism and a Nicol prism. The Wollaston prism is used to split the light into two beams of polarized light at right angles to each other, and the Nicol prism is used to change the relative intensities of light on the standard surface and the specimen. The light reflected from the standard is automatically balanced with that reflected from the specimen by rotation of the Nicol prism. The difference in the amount of reflection between the standard and the unknown surface is indicated by the amount of rotation of the Nicol prism. The test is repeated for each narrow band, and a complete curve is obtained in this way showing the relative or apparent reflectivity of the paper compared with that of magnesium oxide.

Abridged Spectrophotometry. In abridged spectrophotometry, a prism and slit arrangement is not used to isolate the light according to wavelength, but instead a series of filters (usually 8–9) are used to isolate narrow spectral bands. Wratten filters widely used for this purpose cover the ranges given in Table XVIII.

TABLE XVIII

RANGES COVERED BY COLOR FILTERS USED IN ABRIDGED SPECTROPHOTOMETRY

Wratten filter number	Approximate wavelength of maximum response (millimicrons)
76	445
49	455
75	490
74	530
73	570
72	605
71A	630
70	680

Abridged spectrophotometry differs from true spectrophotometry in that the spectral bands are not so narrow, and measurement is made at only a few points on the color scale. The results are not as accurate as those obtained in regular spectrophotometry, but are suitable for many purposes.[171–173] Abridged spectrophotometry can be carried out with the Hunter Multipurpose Reflectometer or the General Electric reflection meter.

Color Specification by the I.C.I. System. The interpretation of color by the spectrophotometer differs from that given by the human eye because the eye measures the density of color and the spectrophotometer does not. The eye tends to average the result so that two samples may look

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[171] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 104,* No. 19: 255–267 (May 13, 1937)

[172] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 104,* No. 20: 271–275 (May 20, 1937)

[173] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 104,* No. 18: 245–251 (May 6, 1937)

alike to the eye, even though they have different spectrophotometric curves. Since there is no clear relationship between physically measured light and the manner in which the human eye sees and interprets light, it is impossible to obtain a true mental picture of color from a spectral reflectance curve alone. In other words, the spectrophotometer does not measure color, but rather the properties which are responsible for color.

In order to specify color, the spectral reflectance curve must be assessed in relation to the visual efficiency of the eye. Visual efficiency, as well as chromaticity, can be calculated from spectrophotometric data, as will be described in the following sections. In the I.C.I. color system, three values are used which are somewhat similar to those used in the Munsell system. These are dominant wavelength (hue), excitation purity (saturation), and visual efficiency (visual brightness). These are objective measurements, in contrast to the subjective properties of the Munsell system.

Tristimulus System. In specifying color psychophysically, it is assumed that the eye reacts as if it contained three sets of color nerves. It is assumed that color is interpreted through the response of the eye to excitation of its three-color nerves by a physical stimulus. The problem of color matching, then, becomes one of matching the stimulus exciting the color. The stimulus can be matched by combining three primary colors, red, green, and blue, called the tristimulus values.

The tristimulus values of the stimulus exciting the color can be determined in a colorimeter by manual adjustment of the relative amounts of the three primaries required to obtain a color match with the sample, using a divided field.[174] Such a match is valid, however, only for the particular observer and for the particular conditions of illumination. It is impossible to establish a positive relationship between the color sensation and the physical properties of the color in this way, because color is a subjective property which depends upon the observer. In order to establish a standard method for computing the sensation produced by a given physical stimulus, the International Commission on Illumination (I.C.I.) established the standard observer at a meeting held in Cambridge, England, in 1931.

Standard Observer. The hypothetical standard observer is based upon the average color matches obtained by a number of observers in England who were known to have normal color vision. The use of the standard observer makes it possible to compute universally accepted color sensation from the physical specification.

Three sets of color data are used to represent the spectral sensitivity of each set of color nerves. One set has its maximum sensitivity in the blue region, another in the green, and another in the red, as shown by the color curves in Figure XVI-22.[174] These color curves can be used to compute the sensation evolved by a given physical stimulus by (*1*) multiplying the spectral energy distribution curve of the standard white light by the spectral reflectance curve of the colored paper to obtain a curve showing the energy distribution of the reflected light and (*2*) multiplying the resulting curve by the three sensitivity curves (Fig. XVI-22) to get three new curves representing the degree to which each individual set of nerves is stimulated.

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[174] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 105,* No. 19: 293–306 (Nov. 4, 1937)

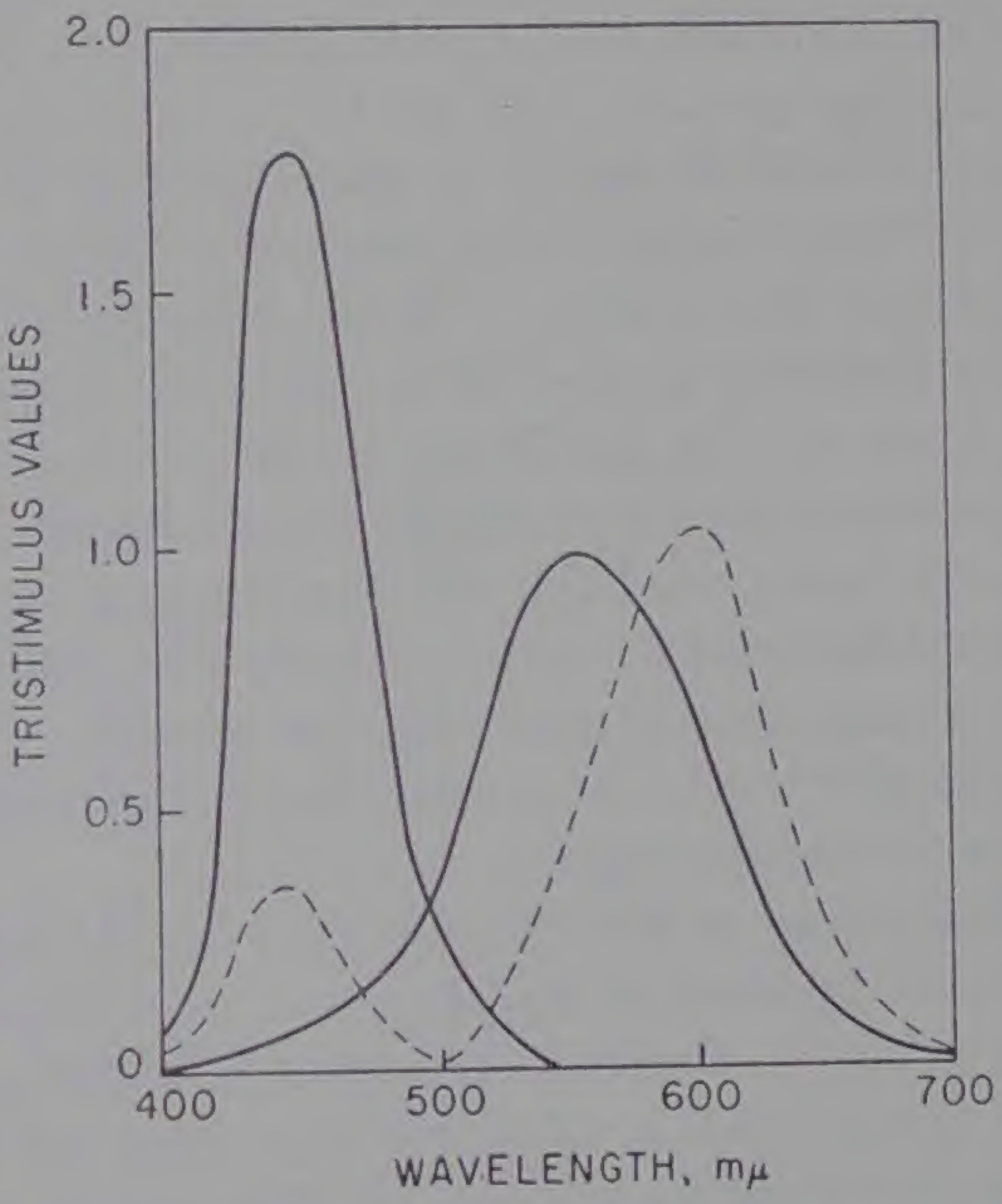

Fig. XVI-22. Tristimulus distribution functions of three primary stimuli.

As used in the I.C.I. system, the standard observer consists of three functions of wavelength which show the relative amounts of three primary stimuli required to match the color of various parts of the theoretical equal energy spectrum. The tristimulus system of color specification is based on four chosen stimuli of homogeneous radiant energy given in Table XIX,

TABLE XIX[174a]

STANDARD COORDINATE SYSTEM

Four chosen stimuli	Coordinates of system		
	X	*Y*	*Z*
700	0.73467	0.26533	0.00000
546.1	0.27376	0.71741	0.00883
435.8	0.16658	0.00886	0.82456
Standard illuminant *B* (approx. mean norm sunlight)	0.34842	0.35161	0.29997

[174a] *Handbook of Chemistry and Physics.* Chemical Rubber Publishing Co., Cleveland.

together with the coordinates used for specifying the system. The standard observer is determined by three distribution functions, $\bar{x}$, $\bar{y}$, and $\bar{z}$, corresponding to the three theoretical primaries represented by the curves in Figure XVI-22, or by three trichromatic coefficients, x, y, and z, which are fractional values defined as follows:

$$x = \bar{x}/\bar{x}, \bar{y}, \bar{z}$$
$$y = \bar{y}/\bar{x}, \bar{y}, \bar{z}$$
$$z = \bar{z}/\bar{x}, \bar{y}, \bar{z}$$

Table XX gives the trichromatic coefficients and distribution functions for equal energy for each wavelength interval of 5 millimicrons.

The information in Table XX is useful because it makes it possible to calculate the tristimulus specification from the spectrophotometric curve. This is done by summing throughout the visible spectrum the product obtained by multiplying the spectral reflectance curve by the spectral energy of the illuminant by the respective spectral distribution functions, $\bar{x}$, $\bar{y}$, and $\bar{z}$, of the standard observer at the appropriate wavelength.[175]

Chromaticity Diagram. The information in Table XX makes it possible to construct chromaticity diagrams using x as the abscissa and y as the ordinate, which gives a complete specification of chromaticity. Only x and y need be used as coordinates, since by definition, $x + y + z = 1$, and hence z is specified by difference when x and y are given. A chromaticity diagram for the spectrum colors is given in Figure XVI-23.[174] The points for the I.C.I. illuminants *A*, *B*, and *C* are given in this figure, as well as the designation for a particular green (point *G* on diagram). The solid line connecting the points specifying the spectrum colors is called the spectrum locus. A line connecting two points specifying two different colors may be regarded as the locus of all points specifying colors obtained by mixing the two colors.

Dominant Wavelength and Purity. It is a difficult matter to visualize color in terms of numbers such as represented by the tristimulus values, and hence it is preferred in many cases to use objective measurements of dominant wavelength and purity.

Dominant wavelength is defined as the wavelength of light which must be added to the light of the illuminant to match the stimulus of a given color. It corresponds to the subjective term hue in the Munsell system. Dominant wavelength is determined on the chromaticity diagram in Figure XVI-23 as the wavelength on the spectrum locus obtained by drawing a line through the point representing the particular illuminant used and the point specifying the color. This gives the dominant wavelength, because any color above the dotted line drawn through the illuminant (e.g., point *C* in the diagram)

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[175] R. S. Hunter, "Photoelectric Tristimulus Colorimetry with Three Filters," U. S. Dept. Commerce, Natl. Bur. of Standards C429 (July 30, 1942)

TABLE XX[174a]

TRICHROMATIC COEFFICIENTS AND DISTRIBUTION FUNCTIONS OF THE STANDARD OBSERVER

Wave-length, mμ	Trichromatic coefficients			Distribution coefficients for equal energy		
	x	y	z	$\bar{x}$	$\bar{y}$ (rel. vis.)	$\bar{z}$
380	0.1741	0.0050	0.8209	0.0014	0.0000	0.0065
385	0.1740	0.0050	0.8210	0.0022	0.0001	0.0105
390	0.1738	0.0049	0.8213	0.0042	0.0001	0.0201
395	0.1736	0.0049	0.8215	0.0076	0.0002	0.0362
400	0.1733	0.0048	0.8219	0.0143	0.0004	0.0679
405	0.1730	0.0048	0.8222	0.0232	0.0006	0.1102
410	0.1726	0.0048	0.8226	0.0435	0.0012	0.2074
415	0.1721	0.0048	0.8231	0.0776	0.0022	0.3713
420	0.1714	0.0051	0.8235	0.1344	0.0040	0.6456
425	0.1703	0.0058	0.8239	0.2148	0.0073	1.0391
430	0.1689	0.0069	0.8242	0.2839	0.0116	1.3856
435	0.1669	0.0086	0.8245	0.3285	0.0168	1.6230
440	0.1644	0.0109	0.8247	0.3483	0.0230	1.7471
445	0.1611	0.0138	0.8251	0.3481	0.0298	1.7826
450	0.1566	0.0177	0.8257	0.3362	0.0380	1.7721
455	0.1510	0.0227	0.8263	0.3187	0.0480	1.7441
460	0.1440	0.0297	0.8263	0.2908	0.0600	1.6692
465	0.1355	0.0399	0.8246	0.2511	0.0739	1.5281
470	0.1241	0.0578	0.8181	0.1954	0.0910	1.2876
475	0.1096	0.0868	0.8036	0.1421	0.1126	1.0419
480	0.0913	0.1327	0.7760	0.0956	0.1390	0.8130
485	0.0687	0.2007	0.7306	0.0580	0.1693	0.6162
490	0.0454	0.2950	0.6596	0.0320	0.2080	0.4652
495	0.0235	0.4127	0.5638	0.0147	0.2586	0.3533
500	0.0082	0.5384	0.4534	0.0049	0.3230	0.2720
505	0.0039	0.6548	0.3413	0.0024	0.4073	0.2123
510	0.0139	0.7502	0.2359	0.0093	0.5030	0.1582
515	0.0389	0.8120	0.1491	0.0291	0.6082	0.1117
520	0.0743	0.8338	0.0919	0.0633	0.7100	0.0782
525	0.1142	0.8262	0.0596	0.1096	0.7932	0.0573
530	0.1547	0.8059	0.0394	0.1655	0.8620	0.0422
535	0.1929	0.7816	0.0255	0.2257	0.9149	0.0298
540	0.2296	0.7543	0.0161	0.2904	0.9540	0.0203
545	0.2658	0.7243	0.0099	0.3597	0.9803	0.0134
550	0.3016	0.6923	0.0061	0.4334	0.9950	0.0087
555	0.3373	0.6589	0.0038	0.5121	1.0002	0.0057
560	0.3731	0.6245	0.0024	0.5945	0.9950	0.0039
565	0.4087	0.5896	0.0017	0.6784	0.9786	0.0027
570	0.4441	0.5547	0.0012	0.7621	0.9520	0.0021
575	0.4788	0.5202	0.0010	0.8425	0.9154	0.0018
580	0.5125	0.4866	0.0009	0.9163	0.8700	0.0017
585	0.5448	0.4544	0.0008	0.9786	0.8163	0.0014
590	0.5752	0.4242	0.0006	1.0263	0.7570	0.0011
595	0.6029	0.3965	0.0006	1.0567	0.6949	0.0010
600	0.6270	0.3725	0.0005	1.0622	0.6310	0.0008

Table continued

TABLE XX (*continued*)

Wave-length, mμ	Trichromatic coefficients			Distribution coefficients for equal energy		
	x	y	z	$\bar{x}$	$\bar{y}$ (rel. vis.)	$\bar{z}$
605	0.6482	0.3514	0.0004	1.0456	0.5668	0.0006
610	0.6658	0.3340	0.0002	1.0026	0.5030	0.0003
615	0.6801	0.3197	0.0002	0.9384	0.4412	0.0002
620	0.6915	0.3083	0.0002	0.8544	0.3810	0.0002
625	0.7006	0.2993	0.0001	0.7514	0.3210	0.0001
630	0.7079	0.2920	0.0001	0.6424	0.2650	0.0000
635	0.7140	0.2859	0.0001	0.5419	0.2170	0.0000
640	0.7190	0.2809	0.0001	0.4479	0.1750	0.0000
645	0.7230	0.2770	0.0000	0.3608	0.1382	0.0000
650	0.7260	0.2740	0.0000	0.2835	0.1070	0.0000
655	0.7283	0.2717	0.0000	0.2187	0.0816	0.0000
660	0.7300	0.2700	0.0000	0.1649	0.0610	0.0000
665	0.7311	0.2689	0.0000	0.1212	0.0446	0.0000
670	0.7320	0.2680	0.0000	0.0874	0.0320	0.0000
675	0.7327	0.2673	0.0000	0.0636	0.0232	0.0000
680	0.7334	0.2666	0.0000	0.0468	0.0170	0.0000
685	0.7340	0.2660	0.0000	0.0329	0.0119	0.0000
690	0.7344	0.2656	0.0000	0.0227	0.0082	0.0000
695	0.7346	0.2654	0.0000	0.0158	0.0057	0.0000
700	0.7347	0.2653	0.0000	0.0114	0.0041	0.0000
705	0.7347	0.2653	0.0000	0.0081	0.0029	0.0000
710	0.7347	0.2653	0.0000	0.0058	0.0021	0.0000
715	0.7347	0.2653	0.0000	0.0041	0.0015	0.0000
720	0.7347	0.2653	0.0000	0.0029	0.0010	0.0000
725	0.7347	0.2653	0.0000	0.0020	0.0007	0.0000
730	0.7347	0.2653	0.0000	0.0014	0.0005	0.0000
735	0.7347	0.2653	0.0000	0.0010	0.0004	0.0000
740	0.7347	0.2653	0.0000	0.0007	0.0003	0.0000
745	0.7347	0.2653	0.0000	0.0005	0.0002	0.0000
750	0.7347	0.2653	0.0000	0.0003	0.0001	0.0000
755	0.7347	0.2653	0.0000	0.0002	0.0001	0.0000
760	0.7347	0.2653	0.0000	0.0002	0.0001	0.0000
765	0.7347	0.2653	0.0000	0.0001	0.0000	0.0000
770	0.7347	0.2653	0.0000	0.0001	0.0000	0.0000
775	0.7347	0.2653	0.0000	0.0000	0.0000	0.0000
780	0.7347	0.2653	0.0000	0.0000	0.0000	0.0000
Totals				21.3713	21.3714	21.3715

may be regarded as a mixture of the illuminant and a spectrum color. Thus, in Figure XVI-23, the dominant wavelength for the color green represented by the point *G* is 500 millimicrons for I.C.I. illuminant *A* and 520 millimicrons for illuminant *C*, based on the standard observer.

Excitation purity is defined as the per cent departure from a neutral gray for a particular illuminant. Excitation purity can be objectively determined from the chromaticity diagram as a ratio of the distance between the points specifying the illuminant and the sample color to the distance between the points specifying the illuminant and the dominant wavelength of the sample color. In Figure XVI-23, the purity is $(C-G)/(C-520)$, which is 25.8%. A purity of 100% means that only light of the dominant wavelength is reflected.

Visual Efficiency. For all practical purposes in color matching, it is usually enough to obtain a close correlation with the dominant wavelength of the specimen and the sample to be matched, as shown by the spectrophotometric curves; then, if the samples have the same approximate purity and visual efficiency, the match will be satisfactory. For very exact work, however, the chromaticity (dominant wavelength and purity) and visual efficiency should be accurately determined. The methods of calculating dominant wavelength and purity have just been described above. Visual efficiency can be calculated in similar manner from spectrophotometric data using values from the standard observer. Visual efficiency defines the true lightness or brightness of the paper and is an important characteristic which is very useful for purposes other than specifying the color.

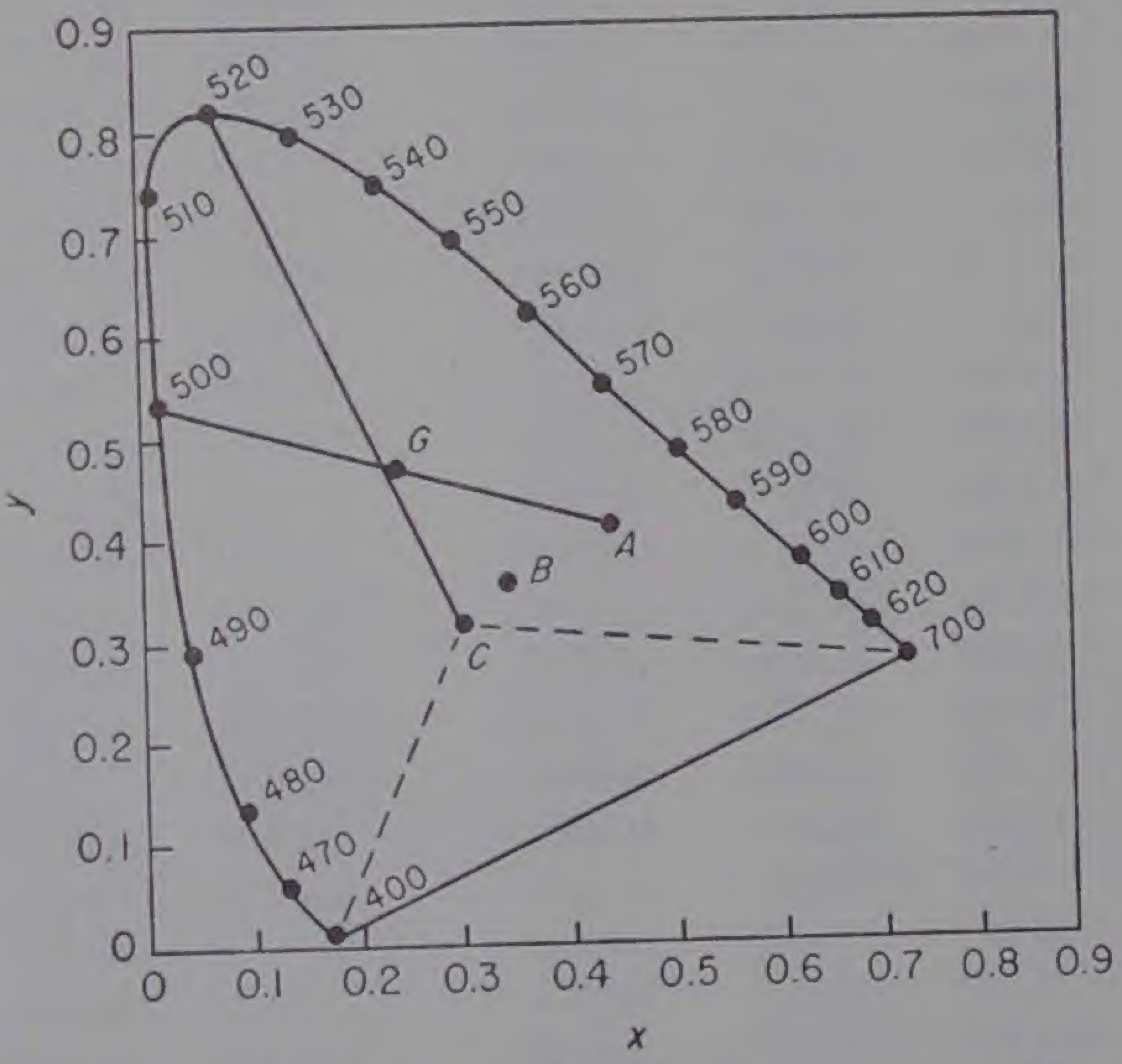

Fig. XVI-23. Chromaticity diagram showing the x and y values of the spectrum colors, I.C.I. illuminants A, B, and C, and a particular green (G).

Visual efficiency is defined as the ratio of the luminosity of the light reflected from the specimen to the luminosity of the light reflected from a perfect, diffuse reflecting body. The relative luminosity of light reaching the eye is determined by the sum of the product throughout the visible spectrum of the spectral energy of the light falling on the sample, the spectral reflectance of the sample, and the luminosity of the light, all at unit wavelength intervals. The relative luminosity of light reflected from the standard body is determined by the sum of the product throughout the visible spectrum of the spectral energy of the light falling on the standard times the luminosity of the light, all at unit wavelength intervals. In practice, relative luminosity rather than absolute luminosity is used, since only the relative spectral energy distribution of the light is known.

In practice, visual efficiency of paper based on the standard observer can be determined by taking the reflectance reading at regular intervals of wavelength on the spectrophotometric curve, multiplying each reading by the corresponding $\bar{y}$ value of the distribution coefficients for that wavelength, and averaging the results throughout the entire spectrum. The $\bar{y}$ value can be used in this way because it was chosen so that it is identical to the standard visibility function (see Fig. XVI-20 and Fig. XVI-22). Values for $\bar{y}$ for the various wavelengths can be obtained from Table XX.

Three-Filter Colorimetry. It has just been explained how color can be completely specified by trichromatic coefficients, visual efficiency, dominant wavelength, and excitation purity, using spectrophotometric data. This method of color analysis yields an accurate specification of the color, but has the disadvantage of requiring considerable time for making the measurements and integrating the results. In order to speed up the work, three-filter colorimetry is sometimes used. This is much more rapid than spectrophotometric colorimetry because the integration with respect to wavelength is done automatically by using special filters. Three-filter colorimetry is not, however, as accurate as spectrophotometric colorimetry, because the photometric conditions (light, filter, and photocell) used in three-filter colorimetry are not spectrally equivalent to the desired combination of standard illuminant and standard observer of the I.C.I., and hence do not yield a true measure of the color. Three-filter colorimetry does serve, however, to fill an important practical purpose.[175]

The three filters generally used in three-filter colorimetry are green, amber, and blue. In making determinations, reflectance measurements are made on the unknown sample relative to magnesium oxide using the three filters. The $\bar{x}$, $\bar{y}$, and $\bar{z}$ values for the I.C.I. scales can be obtained from the following relationships, where *A*, *B*, and *G* represent the readings obtained with the amber, blue, and green filters, respectively. The reading obtained with the green filter closely duplicates the $\bar{y}$ (visibility function) in the tristimulus value.

$$\bar{x} = 0.80A + 0.18B$$

$$\bar{y} = 1.00G$$

$$\bar{z} = 1.18B$$

$$\Sigma = \bar{x} + \bar{y} + \bar{z}$$

$$x = \frac{\bar{x}}{\Sigma}$$

$$y = \frac{\bar{y}}{\Sigma}$$

$$z = \frac{\bar{z}}{\Sigma}$$

$x + y + z$ should equal 1.0

It should be borne in mind that the color match is valid only for the specific illuminant used.

Calibration of the instrument and filter set-up can be made against working standards which should be spectrally similar to the samples to be tested. A wide range of working standards in gray and colored papers are available which have known tristimulus values.[176, 177] The readings which should be obtained for the amber (A), green (G), and blue (B) filters, using the values of the working standards, should be as follows:

$$A = 1.25\bar{x} - 0.19\bar{z}$$
$$G = \bar{y}$$
$$B = 0.852\bar{z}$$

Yellowness is sometimes expressed in three-filter colorimetry as the difference between the reflectance obtained with the amber (A) filter and the reflectance obtained with blue (B) filter divided by the reflectance obtained with green (G) filter—i.e., yellowness equals $[(A–B)/G] \times 100$.

Brightness of Paper (R_∞)

True brightness refers to the lightness or over-all reflectivity, i.e., visual efficiency, of the paper. As shown in the previous section, this is a function of the over-all spectral reflectance of the paper, the energy distribution of the illuminant, the viewing conditions, and the characteristics of the viewer. While visual efficiency is a function of the reflectance over the visible spectrum, papermaker's brightness, on the other hand, is based on a measurement of the reflectance of light from white or near-white papers at a single wavelength in the blue region of the spectrum, that is, light having a wavelength of 457 millimicrons.

Methods of Measuring Brightness. The instruments commonly used for measuring brightness in the paper industry are the General Electric, Hunter, and the Photovolt.

The General Electric instrument employs a null method. Light from a single source is directed along two different paths to two photoelectric cells which are connected with opposite polarities to the terminals of a galvanometer; the amount of light along these two paths is varied by mechanical means until the cells produce the same currents as indicated by a balancing of the galvanometer. The instrument is operated as follows. The glass working standard is placed over the opening and the dial (iris diaphragm) set to read the calibrated brightness of the standard; the standard is then removed and the unknown sample is placed over the opening and the galvanometer balanced with the other dial (sector diaphragm); the standard is then placed over the opening a second time and the first dial (iris dia-

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[176] Munsell Color Company, Baltimore, Maryland

[177] *J. Optical Soc. America*, p. 609 (Dec., 1940)

phragm) is again balanced to give the brightness reading. In making the brightness determination, a thick opaque pad of the test paper is used. The sheets are cut to a size of 2 × 1½ in. (the shortest dimension being in the machine direction) and the pads inserted in the brightness tester with the felt side facing the instrument and the machine direction parallel to the plane of the incident and reflected rays of light. The percentage reflection (based on magnesium oxide as 100.0) is then reported to the nearest 0.1%. Samples should, of course, be used which are free of all blemishes and flaws.

The General Electric instrument in routine use should be in calibration with a master instrument of particular type and design which must be completely specified as to its spectral, geometrical, and photometrical characteristics.[178, 179] In the master instrument, the effective wavelength (457 ± 0.5 millimicrons) is obtained by a suitable combination of glass optics, lamp, filters, and photoelectric cell. The spectral energy distribution is defined to control the rate of absorption of energy in the test specimen and to control the intensity of ultraviolet light. The mean angle of incidence of rays upon the test specimen are maintained at 45° ± 1°, and the mean angle of reflected rays and the incident rays is maintained between 0 and 1° with the normal. These and other characteristics of the master instrument are completely specified to measure correctly at all times the brightness of paper relative to that of freshly prepared magnesium oxide. In calibrating the General Electric instrument used for routine work, both secondary and working standards (which have been standardized against the master instrument) are used. The secondary standards consist of about five pads of paper ranging in brightness value from 60 to 85. At least two working standards made from white opaque glass are also used. During calibration, the instrument is checked against the assigned values of the secondary (paper) standards and adjusted so that the readings of these standards against the working standards agree with the assigned values. The instrument should give the proper reading on all five or six of the secondary standards. Calibration should be done every one or two months. If a different instrument (not the same as the master instrument in design) is used, the readings may not agree with both the secondary and working standards. For these instruments, only the secondary (paper) standards should be used for calibrating the instrument. Working standards can then be evaluated by the instrument in terms of the paper standards.

The Hunter instrument, like the General Electric, is based on a null method. A comparison standard is kept in one beam and the unknown specimen is compared with the standard in a second beam. Several working standards are used covering a wide range of brightness readings. In

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[178] See TAPPI Standards

[179] Such an instrument is maintained by the Institute of Paper Chemistry, Appleton, Wisconsin.

operation, the working standard is placed over the test opening, the scale set at the calibrated reading, and the galvanometer is adjusted to zero by moving a mirror in the circuit closer or farther away from the photocell. With the instrument thus adjusted, the unknown sample is then substituted over the opening and the scale (which moves the photocell in the other circuit closer or farther away from the reflectance surface) adjusted to a null reading on the galvanometer. The brightness reading is then read directly from the scale. The scale reading is based upon the inverse square law which states that the intensity of illumination varies inversely as the square of the distance from the source.

In the Photovolt, a single photocell is used. The instrument must be adjusted before use by placing the search unit over a black cavity, setting the galvanometer to zero, and then placing the search unit over a calibrated standard and adjusting to the correct reading. When properly adjusted in this way, the search unit is then placed on the unknown specimen and the brightness is read directly. Calibration charts should be used with this instrument, since the response of the photocel-galvanometer is nonlinear. The instrument is sensitive to frequency variation in power supply and is subject to error resulting from specular reflectance.[179a]

Importance of Brightness. The practicality of measuring brightness as reflectance at a single wavelength is based on the fact that pulps of the same type have spectral reflectance curves of similar shape, and hence a reading at a single wavelength is sufficient indication of the shape of the curve. Papermaker's brightness is not a complete designation of the color of paper, but is a highly useful arbitrary means for measuring the color quality of white papers. Brightness readings correlate reasonably well with the lightness of the paper and nearly always correlate well with a visual rating of samples if the samples have spectral reflectance curves of similar shape. In order for the brightness reading to be of value in the grading of different papers, the samples must have a similarity in shape of their reflectance curves, and there must be relatively small deviation from neutrality of the colors involved.[180] If samples of pulp of unknown origin are being tested, a complete spectrophotometric curve should be taken, but for ordinary mill testing of papers of known history, a brightness reading is satisfactory. A difference in brightness of 1 to 2 points is considered significant.

It is possible to have two papers equal in papermaker's brightnes which differ widely in "whiteness" and visual efficiency. Subjective grading of samples for brightness does not always agree with the grading obtained on brightness meters. Brightness, as interpreted visually, is a psychological combination of purity and true brightness, purity (percentage deviation from a neutral gray) dominating if the physical differences in brightness are small. Neither papermaker's brightness nor even true visual efficiency always correlates with what most people select as the whitest paper. This discrepancy is due to the fact that a pleasing white is not always the one with the highest degree of whiteness. For example, certain slightly tinted "white" papers may appear more pleasing and "whiter" to the eye than other papers of equal brightness. A pleasing shade of white depends upon the personal preferences for hue, most people preferring a blue-white containing a slight amount of red. An analysis of two white papers was found to be as follows:

[179a] L. R. Dearth, J. A. Van den Akker and W. A. Wink, *Tappi 33,* No. 10: 85A–89A (Oct., 1950)

[180] M. N. Davis, *Paper Trade J. 111,* No. 14: 184–188 (Oct. 3, 1940)

	Paper No. 1	Paper No. 2
Papermaker's brightness (457 mμ)	74.3	77.4
Reflectance of white light	82.6	79.3

Paper No. 2, a blue-white, had a higher papermaker's brightness than Paper No. 1, a creamy white, but the latter had a greater visual brightness, as indicated by the greater reflectance of white light. Paper No. 2 would, however, be selected by the average observer as the whiter paper because of the general preference for a blue-white. Color curves on the two papers are shown in Figure XVI-24.

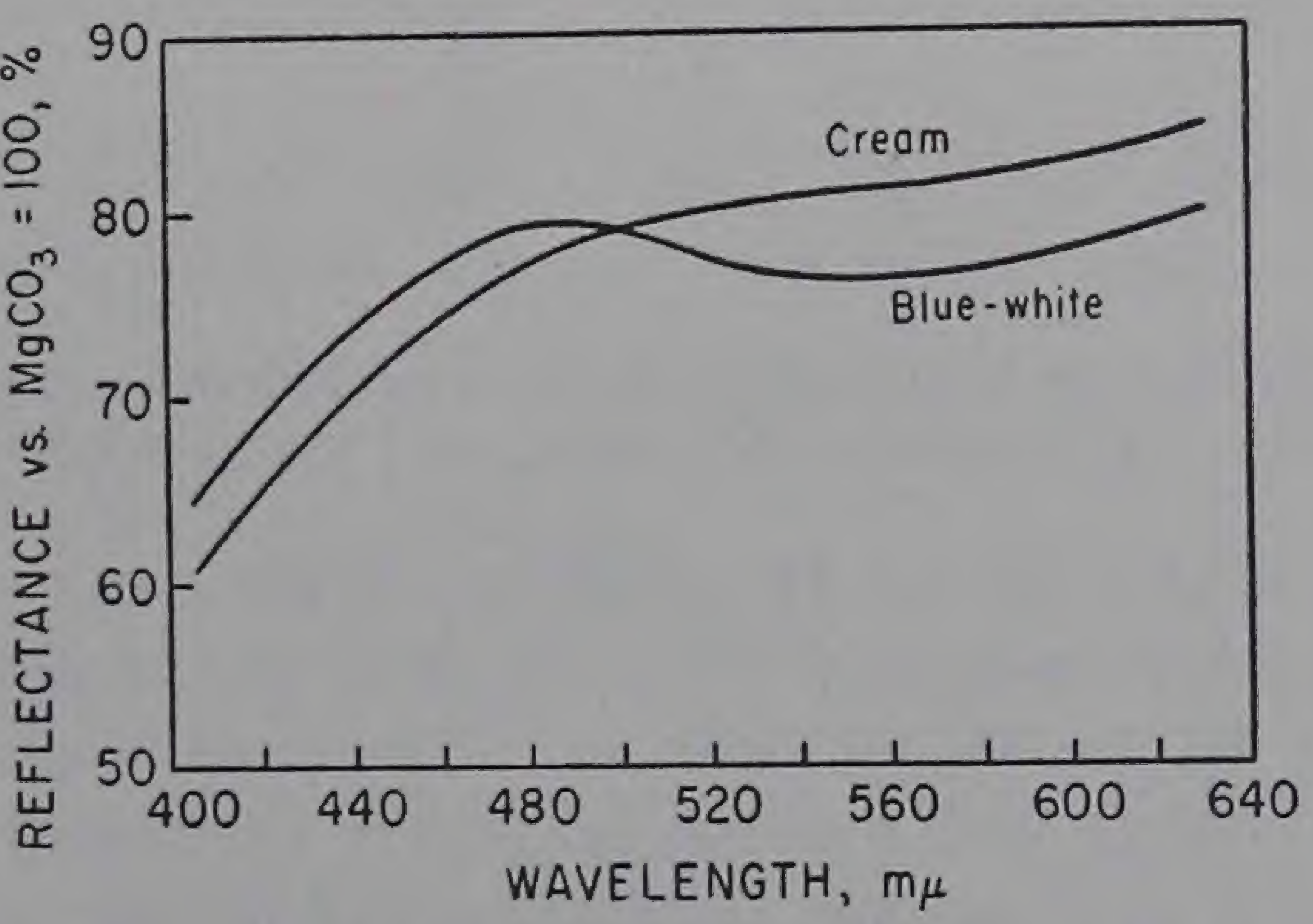

Fig. XVI-24. Spectral reflectivity curves for a cream and a blue-white paper.

Brightness was designed primarily as a test to measure the effectiveness of bleaching in removing the yellowness of pulps, and for this purpose, brightness is admirably suited. The spectral reflectance curve for an unbleached pulp starts off with a relatively low reflectance in the violet end of the spectrum and rises rapidly to a fairly high value in the extreme red end of the spectrum; in other words, an unbleached pulp is a yellow of low purity. Bleaching raises the spectral reflectance curve over the whole range, but the increase is greatest in the blue and violet range where brightness is measured, i.e., in the neighborhood of 457 millimicrons. This makes the brightness reading a particularly sensitive measure of bleaching efficiency.

Spectral reflectance curves showing the effect of bleaching on sulfite and sulfate pulps are shown in Figure XVI-25. Brightness is also well suited for measuring the permanence of paper, since the change in the color of paper on aging or thermal degradation is greatest in the blue and violet regions of the spectrum where brightness is measured. There are isolated cases when brightness readings do not correlate well with the visual efficiency of pulps: for example, in the case of rag pulps made from blue denims which have a bluish tint and consequently have a high brightness reading in relation to their true visual efficiency.

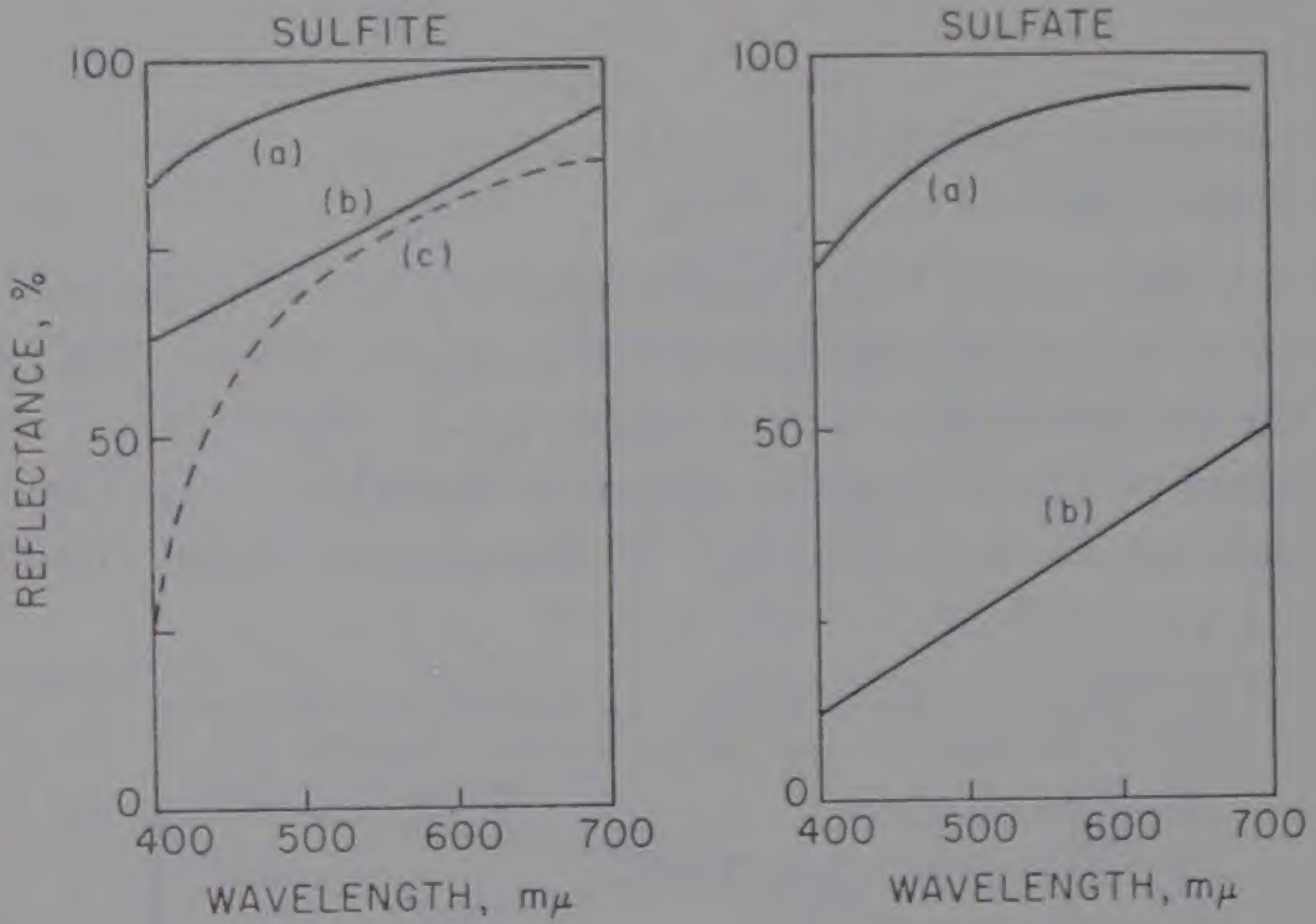

Fig. XVI-25. Effect of bleaching on the spectral reflectance curves of sulfite and sulfate pulps: (a) bleached; (b) unbleached; (c) unbleached groundwood.

Effect of Dyestuffs on Brightness. Brightness readings have no significance on colored papers, particularly those papers which absorb light in the range of 400 to 500 millimicrons. Brightness readings on colored papers rarely correlate with the true brightness (lightness) of the papers.

In practice, a small amount of blue dyestuff or blue pigment is often added to the stock in making white papers, and the effect is pleasant because the average person prefers a blue-white to a yellowish white. However, the brightness is not increased by this practice, since the maximum brightness of any paper is that of the pure pulp. There is no dyestuff which will increase the brightness, since all dyestuffs reduce the amount of reflected light. All dyestuffs must either lower the brightness, increase the opacity, or both.[181]

It is possible to increase the apparent whiteness of paper by adding a dyestuff complementary to the color in the paper, thus graying the paper and making it appear whiter. It is possible to increase the whiteness in this way, even though the total reflectance of the paper is reduced, because paper reflecting only 50% of the light is considered as white. Lewis[182] has presented curves showing the effect of increasing amounts of a special blue dye on the brightness, whiteness, and daylight reflectivity; the brightness remained relatively constant, the daylight reflectivity decreased, and the whiteness increased as the amount of blue dye was increased.

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[181] E. R. Laughlin, *Paper Trade J. 111,* No. 22: 275–281 (Nov. 28, 1940)

As pointed out above, it is possible to tint a given stock without appreciably altering the brightness through the use of dyestuffs which have very little dulling effect.[183] Each dyestuff has a characteristic wavelength where it absorbs more light than others, and this is known as the wavelength of maximum absorption. By choosing dyestuffs which do not affect the reflectance of light of wavelength near that used in determining brightness (i.e., 457 millimicrons), it is possible to tint the paper without appreciably affecting the brightness readings. This is commonly done in tinting white papers.

Reddish blues, violets, and particularly blacks exert the greatest opacifying and dulling influence. Oranges, reds, and greenish blues are of lesser influence and, in some cases, almost without effect.[184] Yellow and green dyestuffs lower the brightness slightly because they absorb an appreciable amount of light in that part of the spectrum from 400 to 500 millimicrons. On the other hand, certain blue dyes (e.g., Halopont brilliant blue) may be added until the reflectance has been decreased as much as 30% at the maximum absorption wavelength (560 millimicrons) before there is any appreciable reduction in reflectance at the wavelength (457 millimicrons) where brightness is measured.[184]

Effect of Pigments on Brightness. The presence of pigments has a marked effect on the brightness of paper. Colored pigments have much the same effect as dyestuffs. Ochre has a particularly bad effect on brightness, since the wavelength of maximum absorption of ochre coincides almost exactly with that at which brightness measurements are made.

Some of the white pigments such as titanium dioxide, calcium carbonate, and zinc sulfide, have much higher reflectivity than pulp fibers, and consequently appreciably increase the brightness of paper. In some cases, fillers tend to concentrate in the upper layers of the paper, thereby resulting in brightness differences as high as 2 to 3 points between the two sides of the sheet. If the pigment is used in a surface coating, marked increases in brightness are obtained.

Relationship between Transparency and Brightness. Increasing the transparency of paper reduces the brightness, because increased transparency means fewer interfaces for the reflection of light, but greater opportunity for the absorption of light. It follows from the above that increasing the density of paper reduces brightness because it increases the transparency. Glassine, for example, has a much lower brightness than ordinary opaque papers, even though the same furnish is used in both cases. Doughty[185] reports a drop in daylight reflectance of 5 to 10% for an increase in solid fraction of 0.2 to 0.5.

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[182] L. C. Lewis, *Paper Trade J. 103,* No. 22: 323–330 (Nov. 26, 1936)

[183] E. R. Laughlin and O. Kress, *Paper Trade J. 100,* No. 8: 106–118 (Feb. 21, 1935)

[184] E. R. Laughlin, *Paper Trade J. 111,* No. 22: 275–281 (Nov. 28, 1940)

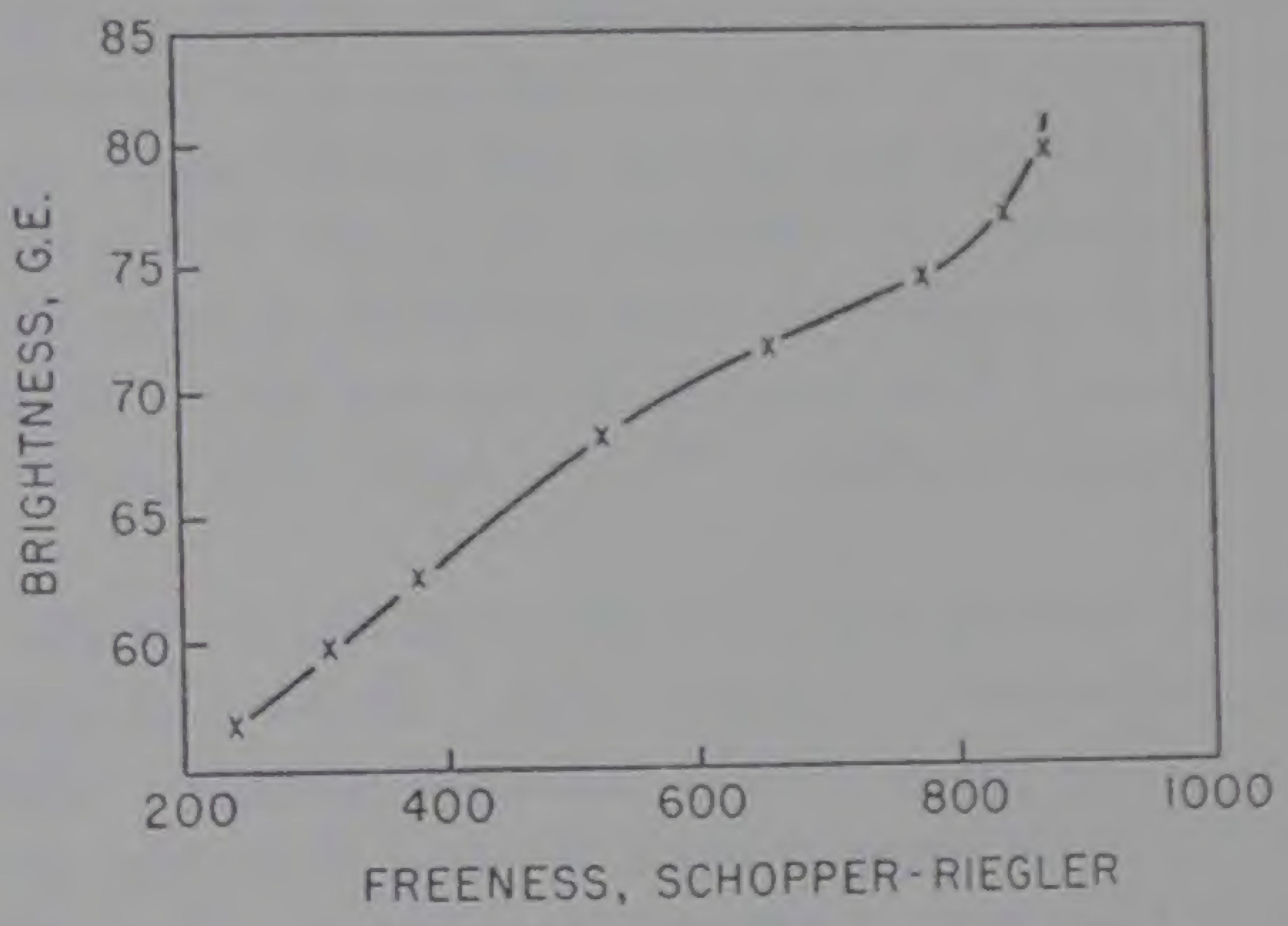

Fig. XVI-26. Effect of beating on brightness.

Beating lowers the brightness, as shown in Figure XVI-26, because of the increase in transparency of the paper resulting from increased beating. Wet pressing appreciably affects brightness. It is important to maintain constant wet pressing conditions when making laboratory handsheets for bleachability determinations in order to eliminate the effect of wet pressing on the brightness of the test sheets. Blackening or loss of brightness on calendering is caused by an increase in transparency of the paper resulting from a reduction in the number of cellulose-air interfaces. The areas which appear dark to reflected light are the areas of highest translucence. The loss of brightness resulting from overcalendering is always accompanied by a loss in opacity. The loss in brightness on supercalendering varies from 1 to 4 points, depending upon the furnish and calendering conditions.[186]

In the case of lined paperboard, the brightness is dependent upon the opacity and brightness of the liner.[187] The use of pigments in the liner stock increases the brightness of the board in a dual way, by increasing the opacity and by increasing the brightness of the liner. Increasing the basis weight of the liner also increases the brightness of the board because it increases the opacity of the liner, thereby resulting in a better covering-up of the dull filler stock. The use of low brightness filler stock tends to reduce the over-all brightness of paperboard.[188]

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[185] R. H. Doughty, *Paper Trade J. 95*, No. 10: 31–38 (Sept. 8, 1932)

[186] M. N. Davis, *Paper Trade J. 111*, No. 14: 184–188. (Oct. 3, 1940)

[187] W. R. Willets, R. T. Bingham and L. H. Eriksen, *Paper Trade J. 109*, No. 9: 91–94 (Aug. 31, 1939)

Comparison of Pulps for Brightness. The brightness of pulp before any materials are added is a good measure of pulp quality and is almost a fundamental property. It is the most important factor affecting the brightness of the finished paper. If the brighter of two pulps does not produce as white a paper as the other, it is true that the brighter pulp can be made to produce the whiter paper by changing the dye formula.[189]

A definite relationship exists between the lignin content and the brightness of pulps, the effect of lignin being greatest in the region of low lignin content.[190] There are other factors which affect pulp brightness, aside from the intrinsic brightness of the pulp. Dirt specks, finger marks, or other surface imperfections on the test pads used for making the brightness determination will result in low readings. Seasonal variations in the clarity of the water used in forming the paper affect pulp brightness. Aging causes the pulp to become yellow and lose brightness, unbleached pulps and groundwood being particularly bad offenders. Overdrying tends to lower the brightness. Bleaching, of course, greatly increases brightness. On a comparative basis, the brightness of different commercial pulps would be approximately those given in Table XXI.

TABLE XXI

BRIGHTNESS OF DIFFERENT PULPS

Type of pulp	Brightness
Unbleached sulfate	25–45%
Bleached sulfate	70–85%
Unbleached sulfite	50–65%
Bleached sulfite	75–85%
Specially purified pulps	up to 90–94%
Groundwood	55–60%

Brightness values are inadequate for characterizing groundwood (although the test is often used) because of the hue of the pulp. A spectrophotometric curve gives more useful information, or the results may be expressed in terms of brightness, dominant wavelength, and purity.[191] The dominant wavelength for groundwood, both bleached and unbleached, is from 562 to 582 millimicrons, or in other words, the pulps are essentially yellow in hue.[191] The spectral reflectivity curve for groundwood shows distinctive low values in the wavelength range from 400 to 450 millimicrons (see Fig. XVI-25).[192] Groundwood papers having the same brightness as bleached sulfite papers, as measured on a brightness meter, will generally appear yellower because of the greater reflection in the yellow range. Consequently, groundwood papers are generally given a low rating in subjective evaluation, due to lack of purity (yellowness) of the reflected light. However, by using a suitable dye, it is possible to tint groundwood to a color which yields identical subjective and instrumental grading.[193]

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[188] W. R. Willets, R. T. Bingham and L. H. Eriksen, *Paper Trade J. 109,* No. 23: 308–310 (Dec. 7, 1939)

[189] J. A. Van den Akker, P. Nolan and W. A. Wink, *Paper Trade J. 114,* No. 5: 46–52 (Jan. 29, 1942)

[190] W. W. Pigman and W. R. Csellak, *Tech. Assoc. Papers 31:* 393–399 (June, 1948)

[191] R. M. Kingsbury, F. A. Simmons and E. S. Lewis, Forest Products Lab., Paper given at TAPPI Mechanical Pulping Conference, Poland Springs, Maine (Sept. 27–28–29, 1948)

Neutral sulfite semichemical pulps which have been bleached with hypochlorite in the presence of sodium silicate exhibit fluorescence. Because of this fluorescence, these pulps tend to give different brightness readings on different brightness meters.

Brightness of Pulp Mixtures. The effect of blending two pulps on brightness can be worked out experimentally by mixing the pulps in various proportions and determining the resulting brightness, or the results can be calculated using the Kubelka and Munk equation, as will be shown later. Calculated and experimental results generally agree closely, as shown in Figure XVI-27, where the calculated and experimental results of blending bleached sulfite and groundwood pulps are shown. Similar results are shown in Table XXII for mixtures of bleached and unbleached sulfite pulp.

TABLE XXII

BRIGHTNESS OF MIXTURES OF BLEACHED AND UNBLEACHED SULFITE PULPS

Pulp in mixture, %		Observed brightness	Expected brightness on weighted arithmetic average of two pulps in mixture
Bleached sulfite	Unbleached sulfite		
0	100	59.13	—
10	90	60.20	61.23
20	80	61.83	63.33
30	70	62.77	65.43
40	60	63.69	67.53
50	50	66.15	69.63
60	40	67.68	71.73
70	30	70.40	73.83
80	20	72.76	75.93
90	10	76.62	78.03
100	0	80.13	—

It can be seen from Figure XVI-27 and Table XXII that the brightness values (either calculated or experimental) are lower than would be expected from the weighted arithmetic average of the two pulps in the mixture, the greatest difference being obtained at about a 50-50 mixture.[194–196]

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[192] J. A. Van den Akker, H. F. Lewis, G. W. Jones and M. A. Buchanan, *Tappi 32,* No. 4: 187–192 (Apr., 1949)

[193] M. N. Davis, *Paper Trade J. 111,* No. 14: 184–188 (Oct. 3, 1940)

Lower than expected brightness values are obtained in mixing a pulp of low brightness with a pulp of high brightness because the duller pulp always predominates in the mixture.[197] The explanation for the accentuation of the darker-colored fibers in a mixture is due to the greater transparency of the light-colored fibers, which means that a greater percentage of the light falling on the bleached fibers tends to pass through the fibers, whereas a greater percentage of the light falling on the unbleached fibers tends to be absorbed. This accentuates the presence of the more opaque and less bright unbleached fibers.

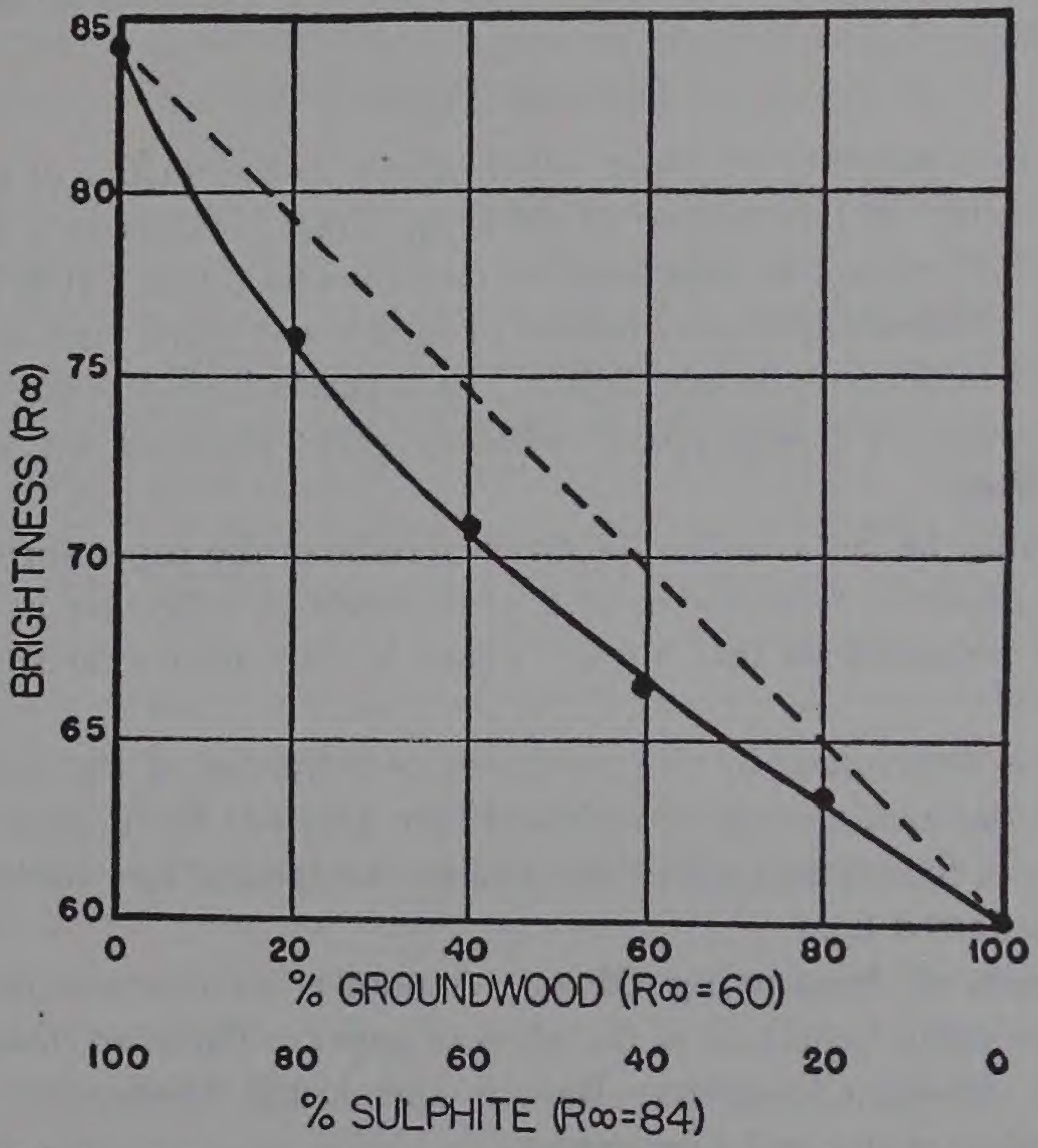

Fig. XVI-27. Effect of mixed furnishes of groundwood and bleached sulfite on brightness: (—) calculated values from Kubelka and Munk equation; (- -) weighted arithmetic average; (●) experimental values. Tappi Data Sheet 147, courtesy Technical Association of the Pulp and Paper Industry.

Because of the above effects, the substitution of bleached groundwood for unbleached groundwood in a mixed furnish with bleached sulfite results

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[194] E. R. Laughlin and O. Kress, *Paper Trade J. 100,* No. 8: 106–127 (Feb. 21, 1937)

[195] W. J. Foote, *Tech. Assoc. Papers 29:* 180–182 (June, 1946)

[196] See TAPPI Data Sheets

[197] E. R. Laughlin, *Paper Trade J. 111,* No. 22: 275–281 (Nov. 28, 1940)

in a greater increase in brightness than would be expected because of the relatively high opacity and covering power of the groundwood, compared with the sulfite. The following example illustrates the point. A 50-50 mixture of bleached sulfite, 80 brightness, and a groundwood, 60 brightness, was found by calculation to have a brightness of 67.3. If the sulfite brightness were increased 10 points, the brightness of the mixture would then become 69.0 (an over-all increase of only 1.7 points). However, if the groundwood brightness were increased 10 points instead of the sulfite, the brightness of the mixture would then become 74.3 (an over-all increase of 7.0 points).

Gloss of Paper

Gloss is a property of paper which refers to the quality of glossiness, luster, or ability of the surface to show an image. Gloss is a qualitative property which cannot be expressed in fundamental terms. It is related to luster (the sudden selective reflection of light) and glare (the undesirable reflection of excessively bright light). In a psychological sense, gloss and luster connote a pleasing effect, whereas glare connotes an unpleasant blinding effect.

Gloss may be described as the characteristic of the paper surface which causes the paper to reflect light at a given angle of reflection in excess of the diffuse reflection at that angle. Gloss is thus related to specular reflectance.

Gloss is determined by (*1*) the index of refraction of the paper which determines the total amount of reflected light and (*2*) the degree of optical smoothness of the surface, which determines the ratio of specularly reflected to totally reflected light.

Methods of Measuring Gloss. A number of instruments measure an arbitrary value indicative of the gloss of paper. These are the Ingersoll Glarimeter, Sheen Glossmeter, Bausch and Lomb Glossmeter, and the Hunter Reflectometer and Glossmeter.

In the Ingersoll Glarimeter, it is assumed that the per cent polarization of the reflected light is a measure of what the eye sees as gloss.[198] The instrument measures contrast or per cent gloss, which is the percentage of regularly reflected light to the total light reflected. In other words, the Ingersoll Glarimeter measures the ratio:

$$\frac{\text{intensity of specular reflection}}{\text{intensity of specular reflection} + \text{intensity of diffuse reflection}}$$

A polarizing prism is used to separate the light into two beams, one containing diffusely and regularly reflected light and the other containing only diffusely reflected light. The amount of polarized light is then compared to the total light by means of a divided field, the two halves of which are made equally bright by rotating an analyzing Nicol prism. The scale reading gives a measure of the glossy reflection as a per cent of the total light reflected. The glarimeter works on an angle of 57½° to the normal on the assumption that maximum polarization occurs at that angle. Another assumption is that the index of refraction of the paper surface is approximately 1.57. This assumption is valid enough in regular papers, but leads to appreciable error in coated papers where the index of refraction may be much higher than this.[199, 200] The glarimeter does not work well in the case of colored papers. Another disadvantage is the subjective nature of the measurements. The instrument works best on papers in the low-gloss range.

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[198] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 104*, No. 2: 19–21 (Jan. 14, 1937)

In the Bausch and Lomb Glossmeter, a beam of light is projected on the test specimen at an angle of 75° to the normal, and the intensity of the light scattered is measured on a photometer at an equal and opposite angle. The Bausch and Lomb Glossmeter measures a value represented by the sum of the intensities of the specular reflection and the diffuse reflection. A piece of polished black glass is used as the working standard. At the incident angle used (75°), polished black glass reflects specularly about 26% of the incident light, but the instrument is adjusted so that the scale reading is 100 with the black glass in place.[201] When a specimen of the paper is placed over the glass standard, the gloss of the paper can be read directly on the meter. A paper which reflects specularly 13% of the incident light will have a gloss of 13/26, or 50% of the gloss of black glass which shows up directly on the scale as a gloss of 50. One advantage of the Bausch and Lomb Glossmeter over the Ingersoll Glarimeter is the lower operating angle used. The ratio of specular to diffuse reflection is over three times as great at 75° (15° operating angle) as it is at 57½° (32½° operating angle).[201] The Sheen Glossmeter is similar to the Bausch and Lomb except that it operates at an angle of 45° instead of 75°.

Gloss can be measured with the Hunter Multipurpose Reflectometer, although the values obtained with one instrument do not duplicate those of another instrument because receptor field angles are not accurately controlled. Reproducible gloss measurements can be obtained on the Hunter Glossmeter. Both specular gloss (sheen) and contrast gloss can be measured with the Hunter Multipurpose Reflectometer. The theoretical primary standard for measuring specular gloss is the perfectly reflecting mir-

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[199] O. Kress and H. W. Morgan, *Paper Trade J. 100,* No. 26: 337–338 (June 27, 1935)

[200] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 104,* No. 2: 19–21 (Jan. 14, 1937)

[201] O. Kress and H. W. Morgan, *Paper Trade J. 100,* No. 26: 337–338 (June 27, 1935)

ror, although such a mirror is not physically attainable. Working standards consist of highly polished pieces of black glass which are accurately calibrated for gloss. In measuring specular gloss, part of the light beam is taken out by means of a mirror and reflected onto the gloss surface at 45° from which it is diverted to the gloss photocell. (Attachments are available for measuring gloss at 60 and 75°.) A semi-diffusing mirror actuated by screw in front of the photocell is used to adjust the fraction of the gloss beam falling on the photocell when the instrument is being standardized. The galvanometer is set at zero when the gloss opening is measured; then a gloss standard is placed over the opening and the galvanometer deflection noted; finally the paper specimen is placed over the opening and the galvanometer deflection again noted. Gloss is determined by:

$$\frac{\text{known gloss of standard surface} \times \text{deflection obtained with paper sample in place}}{\text{deflection obtained with standard surface in place}}$$

Contrast gloss (ratio of specular reflectance to diffuse reflectance) can be measured directly on the gloss scale. This is done by lowering the two mirrors and using only the reflectance opening so that a measurement is made directly of the relative amount of light reflected specularly to the amount reflected diffusely. The reflectometer then furnishes approximate relative values of:

$$\text{contrast gloss} = \frac{\text{apparent reflectance } 45^\circ, -45^\circ}{\text{apparent reflectance } 45^\circ, 0^\circ}$$

This may also be expressed as 1 minus the reciprocal of the above, or

$$\text{contrast gloss} = \frac{\text{apparent reflectance } 45^\circ, -45^\circ - \text{apparent reflectance } 45^\circ, 0^\circ}{\text{apparent reflectance } 45^\circ, -45^\circ}$$

There is no single primary standard for contrast gloss. Calibrated working standards consisting of matte, white porcelain enameled metal plates can be obtained, or a surface painted with white casein paint can be used, since it has a value of contrast gloss near unity.

Contrast gloss describes the extent to which paper departs from mattness. It correlates well with the tendency of paper to produce glare from specularly reflected light. High contrast gloss explains why black papers often appear highly glossy in spite of the fact that the total reflectance is low. For this reason, many chemists advocate reporting gloss as contrast gloss (percentage of specular reflectance to total reflectance), rather than as total specular reflectance. Specular gloss tends to show up differences in printing quality, and it is best adapted for measuring very glossy surfaces (e.g., lacquered papers).

Gloss is often measured visually by comparing two sheets side by side under the same conditions of lighting. In most cases, the sheet is held so that the light falls on the paper at an angle of 45° at the front while being viewed at an angle of 45° from the back.[202] However, easier differentiation can be made by using lower viewing angles because of the increase in specular reflection at low viewing angles. As the angle is lowered down to about 10 to 25°, total reflection increases, specular reflection increases, diffuse reflection decreases, color effect decreases, opacity effect decreases, and smoothness effect increases.[203]

Low viewing angles are particularly desirable in the case of colored paper in order to keep the effect of diffuse reflection to a minimum. For example, a yellow paper which has the same gloss as a blue paper when viewed at an angle (field) of 10 to 20° might show a higher gloss than the blue paper when viewed at an angle of 40°. This is due to the greater diffuse reflection at the higher viewing angle, and the fact that the eye is more sensitive to the yellow color.[204] The viewing angle must not be too low, however, since this makes it difficult to distinguish different samples. Viewing angles less than 5 to 10° are not desirable.[205]

Harrison[206] found that there is a broad linear relation between gloss readings obtained on different samples using the Bausch and Lomb, Ingersoll, and Sheen glossmeters, and the visual gloss determined by a number of different observers. There are, however, substantial and erratic differences between instrumental gloss ratings and visual gloss ratings. The Ingersoll in particular shows poor correlation with visual grading. Kress and Morgan[207] found that the Bausch and Lomb Glossmeter, which depends upon light reflection, correlates much better with visual rating than the polarization type glarimeter when various grades of pigment-coated papers were tested.

Importance of Gloss. Many printers demand a glossy paper because they associate gloss with high surface smoothness and good printing quality. Gloss is associated with high optical smoothness. In order for regular reflection to take place, the height of the irregularities on the reflecting surface must not exceed about one-sixteenth of the wavelength of the incident light.[208]

Gloss does not always go hand in hand with physical smoothness since it is possible to have a glossy surface which is quite rough. Adding sand to a glossy paint, for example, does not reduce the gloss, although it does, of course, make the paint film very rough. However, the average observer unconsciously tends to downgrade the rougher paper, even though the gloss is the same.

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[202] V. G. W. Harrison, *Paper-Maker 118,* No. 2: 106–114, 123 (Aug., 1949)

[203] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 104,* No. 1: 6–9 (Jan. 7, 1937)

[204] *Idem.*

[205] *Idem.*

[206] V. G. W. Harrison, *Paper-Maker 118,* No. 2: 106–114, 123 (Aug., 1948)

[207] O. Kress and H. W. Morgan, *Paper Trade J.* 100, No. 26: 337–338 (June 27, 1935)

[208] R. W. Wood, *Physical Optics,* p. 43, The Macmillan Co., New York, N. Y. (1943)

High gloss is often associated with poor reading quality, due to glare. The ideal surface should catch and reflect the light when the light source is behind the observer and at a high angle of incidence, but should absorb the light when viewed at a low angle with the light source in front. If the paper surface does diffuse the light the same in all directions, it will exhibit glare when the light source is in front of the observer, i.e., a higher proportion of the light will be reflected at the glare angle, thereby leaving less light for the other angles where it is more useful. The proportion of light at the glare angle need not be a great deal greater than the diffuse reflection at that angle in order for the sample to exhibit glare, 4% greater light reflection at the glare angle being sufficient to cause appreciable glare. Gloss can be reduced by coating the paper with highly opaque pigments, provided that the pigment surface is not too highly finished.

Ordinary grades of paper specularly reflect only 0.2% to 6.0% of the light incident upon the paper at an angle of 45°,[209] although certain coated papers may have much higher specular reflectance than this. Typical gloss values for several different grades of paper are given in Table XXIII compared with a standard value of 100 for polished black glass.[210] As previously mentioned, black glass actually reflects specularly only 26% of the incident light at an angle of 45°.

TABLE XXIII

Gloss of Different Papers Compared to Polished Black Glass as 100

Lacquer-coated papers	96
Magazine cover	70
Machine-coated book	51
Supercalendered book	30
English finish book	12
Typewriter bond	6
Mimeograph	4
Household waxed paper	57
Bread wrapper	63

Finish. Finish is a broad term which is used in the paper industry to describe the surface characteristics affecting the appearance and feel of paper. It is a composite property and includes smoothness, softness, gloss, and other less definable properties.

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[209] R. S. Hunter, "A Multipurpose Photoelectric Reflectometer," U. S. Dept. of Commerce, *Natl. Bur. Standards, Research Paper RP 1345* (Nov., 1940)

[210] Technical Bulletin "New Portable 75° Glossmeter," (July, 1949). Measured on Portable glossmeter, Henry A. Gardner Laboratories, 4723 Elm St., Bethseda, Maryland

Because of its complexity, finish cannot be measured or expressed by a single value, and is usually expressed as high, medium, or low, in the opinion of the observer. Other indefinite terms used are smooth finish, glazed finish, English finish, or machine-glazed finish. Pattern is related to finish in that it is a surface characteristic attributed to variation or pattern in color, gloss, or surface smoothness.

With paperboard, it is customary to designate the finish by numbers ranging from 1 to 4; No. 1 finish is a fairly rough surface, and No. 4 finish is the highest possible machine finish. Other definitions are:

(*1*) *Machine finish:* either a high or a low finish, but a finish which is obtained on the paper machine.

(*2*) *English finish:* a special machine finish which is quite high, but which is obtained without too much gloss.

(*3*) *Glazed finish:* a finish obtained by moistening the surface of the paper and then calendering under high pressure.

(*4*) *Machine-glazed finish:* a finish obtained by drying the sheet against a large, highly polished metal drying roll, a Yankee drier.

(*5*) *Smooth finish:* a finish obtained by the use of pressure rolls or a breaker stack in the drier section of the paper machine.

(*6*) *Antique finish:* a rough finish which may be obtained by eliminating all calendering.

Drawing paper is an example of a paper requiring a special finish, since this paper must be fairly rough, but must, at the same time, have a fine grain. Special felts and special methods of drying and calendering are often used to obtain the desired results.

Transmittance of Light

Transmittance of light refers to the ability of paper for passing rays of light through the sheet. There are two ways in which light may be transmitted, by parallel, and by diffuse transmittance. Parallel transmittance refers to the capacity for transmitting rays of light without scattering; diffuse transmittance refers to the capacity for transmitting scattered light. The sum of the diffuse and parallel transmittance gives the total transmittance of the paper.

Opacity is a property of paper which is determined by the total amount of transmitted light (diffuse and non-diffuse). It is defined as the reciprocal of the amount of light transmission; that is, a perfectly opaque paper is one which is absolutely impervious to the passage of all visible light. Opacity is generally measured by the amount of "show through" when the material to be tested is held directly against the object to be viewed.

Transparency is somewhat related to opacity, but differs in that it is determined by the amount of light which is transmitted without scattering. A perfectly transparent material would be one which reflects, refracts, or absorbs none of the light falling on the material, but instead transmits all the light without scattering. If the material has a tendency to scatter light, transparency will vary with the distance between the material and the object being viewed.[211] On the other hand, if the material is non-scattering, vision will be good regardless of the distance between the material and the object being viewed. Hence, transparency is measured by the percentage of small angle transmission of a beam of parallel light when there is a space separating the material and the object being viewed. The transparency ratio, which is the true measure of transparency, is the ratio between the parallel transmittance and the total transmittance. The most transparent paper made (glassine paper) has in the neighborhood of 10 to 40% parallel transmittance for a total transmittance of 60 to 85%. On a comparable basis (65% total reflectance), a tissue paper would have only 3% parallel transmittance.[212] Transparency ratio is the best method of evaluating highly transparent materials, whereas opacity measurements are more suitable for relatively opaque papers.[213]

Between the two extremes of a perfectly opaque and a perfectly transparent paper, there is a state where a part of the light is transmitted. This is known as translucency. Nearly all commercial papers are translucent, that is, they permit the passage of some light. The word "opaque" is loosely used in reference to paper; for example opaque bread wrapper may have an opacity of only 60%, whereas opaque book paper may have an opacity of 90%. The smallest difference in opacity which is perceptible by visual observation is between 0.3 to 0.6 units.[213a]

Methods of Measuring Opacity. Opacity is an important property of printing, bond, and writing papers, and is usually a part of the specification of these papers. The U. S. Government Printing Office has minimum specifications for the opacity of uncoated book papers, ranging from 86 for a 45-lb. book to 90 to 91 for a 60-lb. book (25 × 38—500).

Opacity is a fundamental property which can be accurately determined. In measuring opacity, a photoelectric cell is used to register the amount of reflected light when the paper is backed by an appropriate surface. Opacity can best be measured by contrast ratio, that is, by a ratio of the diffuse reflectance when a single sheet of the test paper is backed by a black body to the diffuse reflectance when a single sheet of the paper is backed by a white body. The reflectance of the paper is generally higher when backed by the white body than when backed by the black body because of the greater amount of transmitted light which is reflected by the white body. If there were no difference in reflection when backed by the white and black bodies, the opacity would be 100%, representing a perfectly opaque paper. If the reflectance were zero when backed by the black body, the opacity would be zero, representing a perfectly translucent paper. The ideal contrast ratio could be obtained by measuring the apparent reflectance of the paper when backed by a perfectly absorbing body (R_0) divided by the apparent reflectance when backed by a body having a perfect or unit reflectance ($R_{1.00}$). A black cavity lined with black velvet having an apparent reflectance less than 0.5% can be used for the R_0 reading, but there is no perfectly reflecting white body, and consequently a body of reflectance lower than 1.00 must be used for white backing. There are two methods of measuring opacity by contrast ratio: (*1*) TAPPI opacity, using a white backing of reflectance of 0.89, and (*2*) printing opacity, using a backing of an opaque pad of the paper under test. These methods of measuring opacity are discussed in the following sections.

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[211] D. B. Wicker, *Paper Trade J. 105*, No. 17: 233–242 (Oct. 21, 1937)
[212] L. C. Lewis, *Paper Trade J. 103*, No. 22: 323–330 (Nov. 26, 1936)
[213] D. B. Wicker, *Paper Trade J. 107*, No. 17: 198–206 (Oct. 27, 1938)
[213a] V. G. W. Harrison and S. R. C. Poutter, *Paper-Maker 119*, No. 6: 416–420, 429 (June, 1950)

When instrumental measurements of opacity are being made, the spectral nature of the light, geometry of illumination and viewing, and the spectral reflectance of the backing body must be specified. For best results, monochromatic light should be used such as that obtained from the green filter used on the photocell in the Bausch and Lomb. Opal-glass standards can be used for standardizing the opacimeter.

Measurement of TAPPI Opacity. TAPPI opacity is the ratio of the reflectance of a single sheet backed by a black body to the reflectance of a single sheet backed by a white body having an absolute effective reflectance of 89%, that is,

$$\text{TAPPI opacity} = R_0/R_{0.89}$$

(The apparent reflectance of the backing white body is 91.5%, which is obtained by dividing the effective reflectance by the absolute reflectivity of magnesium oxide (97%).) A white background of high reflectivity is used in measuring TAPPI opacity in order to obtain high contrast with the reading obtained with the black background. In the Bausch and Lomb Opacimeter, the white backing is not placed in actual contact with the sample, and this, together with other factors, results in white backing having an absolute reflectance of 89%.[214] For bond papers, TAPPI opacity varies from about 80 for light-weight sulfite papers up to about 93 for heavier rag content papers.

Measurement of Printing Opacity. Printing opacity is the ratio of the reflectance of a single sheet of paper when backed by a black body to the reflectance of a thick pad of the paper. The ratio is expressed as R_0/R_∞. Printing opacity measures the same property which is visually judged as show through when a number of sheets printed on one side are stacked in a pile. Printing opacity is nearly always a larger value than TAPPI opacity, since the amount of light returned from a thick pad of the paper is generally less than that returned from the standard white reflector used in measuring TAPPI opacity.

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[214] D. B. Judd, *Paper Trade J. 100,* No. 1: 4-8 (Jan. 3, 1935)

Two different samples may have the same printing opacity and yet have slightly different TAPPI opacity. This occurs when the two samples have very different values of reflecting power for a single sheet and for a pile of sheets, only the ratio of the two reflecting powers remaining constant.[215] The poorest correlation is observed between a white and a gray paper. If a white and gray paper have the same printing opacity, the white paper will have the greater TAPPI opacity. An illustration of a white and a gray paper which have equal printing opacities but unequal TAPPI opacities is shown in Table XXIV.[216] There is a difference of 5% in TAPPI opacity, but no difference in printing ratio, which is 87.5% in both cases.

TABLE XXIV

WHITE AND GRAY PAPER HAVING EQUAL PRINTING OPACITIES BUT UNEQUAL TAPPI OPACITIES

	White paper	Gray paper
R_0	70%	55%
R_∞	80%	63%
TAPPI opacity	84%	79%
Printing opacity	87.5%	87.5%

The above illustration is an extreme case and would not occur in normal testing, since generally only papers of similar brightness are compared for opacity. Ordinarily, there is very close correlation between printing opacity and contrast ratio for most papers.[217] Printing opacity is the preferred test.

Printing opacity is less subject to instrument error than TAPPI opacity because there is no spacing between the sample and the white backing body to affect the effective reflectance of the white body as there is in TAPPI opacity.[218] One of the objections to the use of printing opacity as a test has been the need of a thick pad of the paper for measuring R_∞. However, this objection can be overcome by determining R_∞ by calculation from the R_0 and TAPPI opacity readings, using tables or curves derived from the Kubelka and Munk equation. The means for doing this will be given later.

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[215] M. N. Davis, *Paper Trade J. 93,* No. 16: 181–184 (Oct. 15, 1931)

[216] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 109,* No. 4: 30–36 (July 27, 1939)

[217] M. N. Davis, *Paper Trade J. 93,* No. 16: 181–184 (Oct. 15, 1931)

[218] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 109,* No. 4: 31–36 (July 27, 1939)

Measurement of Printed Opacity. Another type of opacity measurement is printed opacity. This test is made by using a sheet printed on one side with a solid black color for the R_0 reading. The opacity is measured as the ratio of the diffuse reflectance from the uninked side of the printed sheet to the diffuse reflectance of an opaque pad of the unprinted paper. This test is designed to measure the show through which occurs on printing. The results depend upon the amount of penetration of ink and vehicle into the paper, as well as the original opacity of the paper.

Measurement of Opacity by Transmittance. Measurement of opacity by reflected light, as done in the case of printing opacity and TAPPI opacity, is a more useful method of measuring opacity than a measurement by transmitted light. The reason for this is that the opacity of most paper is judged by looking at the paper in reflected light while the paper is backed by a surface covered with light and dark areas. However, in the case of packaging papers, which are used primarily for their light-protecting qualities, it is more suitable to measure opacity by transmission than by reflection of light.

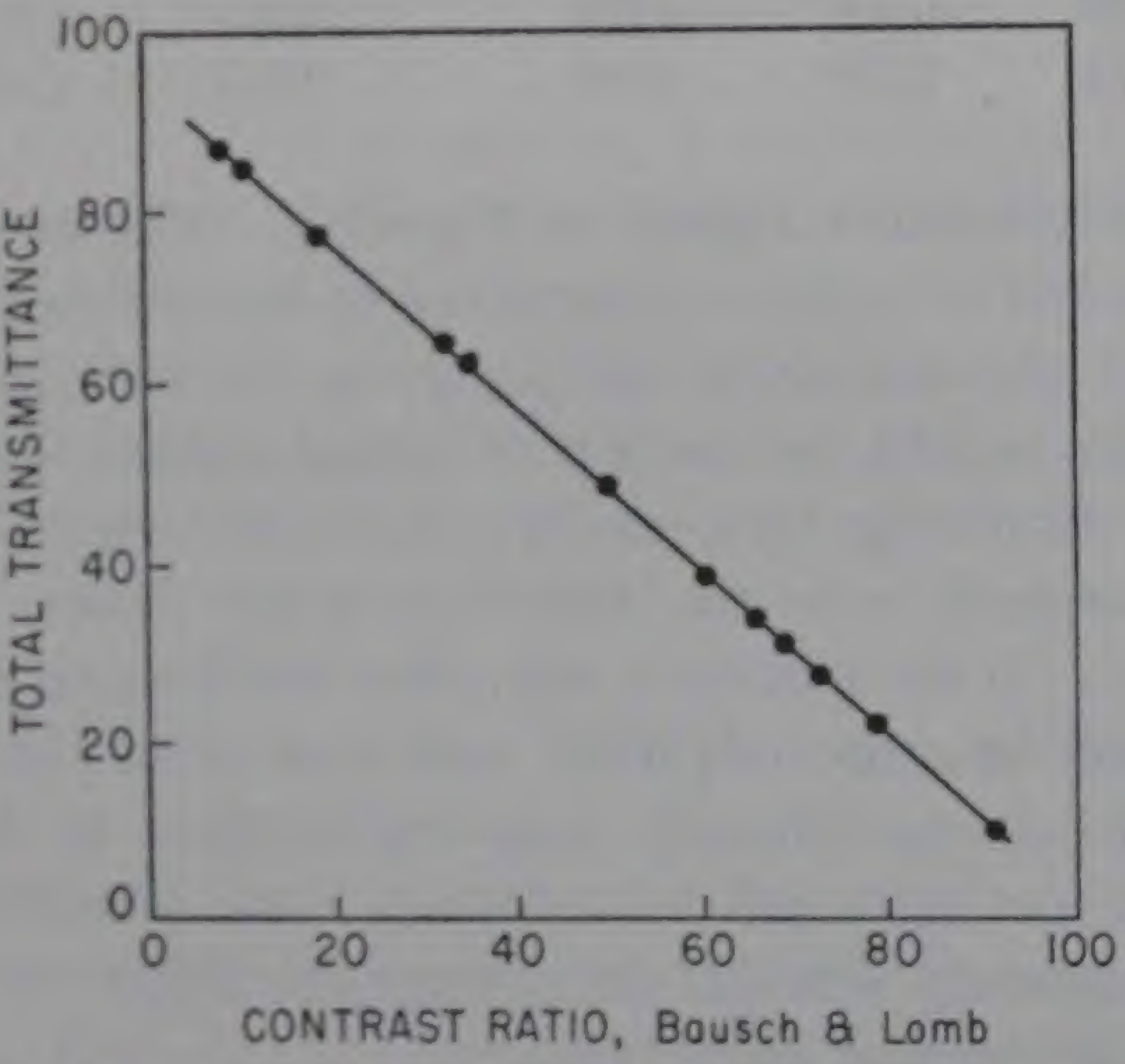

Fig. XVI-28. Relationship between contrast ratio and total transmittance for transparent papers.

In measuring opacity by transmitted light, a sample of paper is placed between a standard light source and a photoelectric cell, and the total amount of light transmitted is compared with the total amount of light falling on the photocell when there is no paper between the light source and photocell. For transparent papers of the same absorptive qualities, there exists an empirical linear relationship between the total transmittance of light and the contrast ratio, as shown in Figure XVI-28,[219] but for ordinary papers there is no simple relationship between opacity as determined by contrast ratio and by transmittance.[220]

Effect of Sheet Weight on Opacity. Increasing sheet weight has the obvious effect of increasing the opacity of the paper. There is, however, a limiting point beyond which further increases in basis weight have no further effect on opacity. The results in Table XXV, taken from Judd,[221] show the effect of increasing basis weight on TAPPI opacity ($R_0/R_{0.89}$) and reflectance over a black backing body (R_0).

TABLE XXV

EFFECT OF BASIS WEIGHT ON OPACITY AND REFLECTANCE

Basis weight 25 × 40—500	Sulfite writing paper ($R_\infty = 0.81$, ash 0.36%)			Book paper ($R_\infty = 0.83$, ash 5.89%)		
	R_0 (Hunter)	Printing opacity (Hunter)	TAPPI opacity	R_0 (Hunter)	Printing opacity (Hunter)	TAPPI opacity
38	0.606	0.747	0.712	0.725	0.877	0.85
46	0.646	0.799	0.768	0.745	0.900	0.88
53	0.677	0.831	0.807	0.769	0.929	0.91
64	0.714	0.881	0.862	0.785	0.947	0.93
75	0.740	0.906	0.887	0.802	0.906	0.95
111	0.778	0.959	0.944	0.821	0.994	0.99

Effect of Refractive Index on Opacity. The amount of light reflected and refracted by paper is determined by the number, size, and shape of the individual constituents of the paper, by the indices of refraction of these constituents, and by the amount of optical contact between these constituents. The scattering between two materials whose surfaces are in optical contact depends upon the difference in the indices of refraction of the two materials. If the indices of refraction for the two materials are the same, no light will be scattered; if the indices of refraction are different, a part of the light passing obliquely from one medium to the other will be bent (refracted) and part will be reflected. The proportion of light reflected at each boundary is larger the greater the difference between the refractive indices of the two materials.

When light within a material of high index of refraction strikes the line of separation between this material and the surrounding medium of low refractive index, part of the light will pass (be refracted) into the surrounding medium, and part will be reflected back into the material. Because the light is going from a material of high index of refraction into a medium of low index of refraction, the light is bent away from the normal at an angle greater than the angle of incidence. As the angle of incidence is increased, the angle of refraction increases so that eventually the refracted ray lies along the line of separation between the material and the surrounding medium. This is known as the critical angle, i.e., the angle of incidence for which the angle of refraction is 90°. All the incident light which strikes at an angle greater than the critical angle will be totally reflected back into the material of high refractive index. The critical angle can be calculated as:

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[219] D. B. Wicker, *Paper Trade J. 107,* No. 17: 198–206 (Oct. 27, 1938)

[220] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 109,* No. 4: 31–36 (July 27, 1939)

[221] D. B. Judd, *Paper Trade J. 106,* No. 1: 39–46 (Jan. 6, 1938)

$$\frac{\text{sine angle of incidence}}{\text{sine angle of refraction }(90^\circ)} = u_2$$

where u_2 is index of refraction of surrounding medium relative to that of the material. Since sine $90^\circ = 1$, $u^2 =$ sine critical angle. Thus, it can be seen that the higher the index of refraction, the greater the critical angle, and the more light which is reflected. This accounts for the high opacifying effect of materials of high refractive index.

Effect of Sheet Density on Opacity. Cellulose absorbs very little light, and consequently a homogeneous sheet of cellulose (e.g., cellophane) is quite transparent. Ordinary paper is not homogeneous, since it is made up of individual fibers separated by air spaces. Consequently, paper has a relatively high opacity.

The fiber area in paper is made up of two components, area which is in optical contact with other fibers and area which is not in optical contact with other fibers. Optical contact exists when two fibers are bonded together in ordinary fiber bonding. The unbonded areas of the fiber are responsible for the scattering of light, since it is only at the fiber-air interfaces that scattering occurs. No scattering or reflection of light occurs when two fibers are in optical contact.

The scattering coefficient of paper (*S* value) is a linear function of the specific surface per unit of mass of the paper,[222, 223] and hence opacity must also be a direct linear function of specific surface, assuming there is no change in absorption (*K* value).[224] Beating would be expected to increase opacity, because beating increases the total surface area of the fibers at which scattering may occur. However, beating also increases the area of optical contact between fibers by increasing the area of fiber bonding, and this tends to reduce the opacity.[225] Pulps of exceptionally high alpha cellulose content tend to increase in opacity on beating because the amount of fiber bonding of these pulps increases very little on beating, whereas the specific surface of the pulp is increased.

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[222] S. R. Parsons, *Paper Trade J. 115,* No. 25: 314–322 (Dec. 17, 1942)

[223] M. N. Davis, *Paper Trade J. 111,* No. 14: 40–44 (Oct. 3, 1940)

[224] The *S* and *K* values are those in the Kubelka and Munk theory.

[225] F. T. Ratliff, *Tappi 32,* No. 8: 357–367 (Aug., 1949)

The fundamental sheet property affecting opacity is the density of the paper. According to Clark,[226] the opacity of paper decreases approximately linearly with increasing solid fraction over most of the commercial range of density. Actually, opacity goes through a maximum with increasing solid fraction, because at very low solid fractions, the paper approaches pure air, which has zero opacity, and at very high solid fractions (approaching 1.0), the paper approaches pure cellulose, which also has zero opacity. Doughty[227] found that opacity goes through a maximum at a solid fraction of 0.3 to 0.5, as shown in Figure XVI-29, when unbeaten spruce sulfite pulp is wet-pressed into sheets of varying solid fraction. Wicker[228] found that the transparency of paper increases rapidly as the solid fraction of the sheet is increased from 60% on upward until eventually the transparency reaches a maximum at a solid fraction of about 90%, which is the practical upper limit. The last 10% of residual air voids places a limitation on the transparency of glassine sheets, since these air voids have an interfering effect on light transmission. Wicker points out that the birefringent nature of cellulose also imposes a limiting transparency less than 100%.

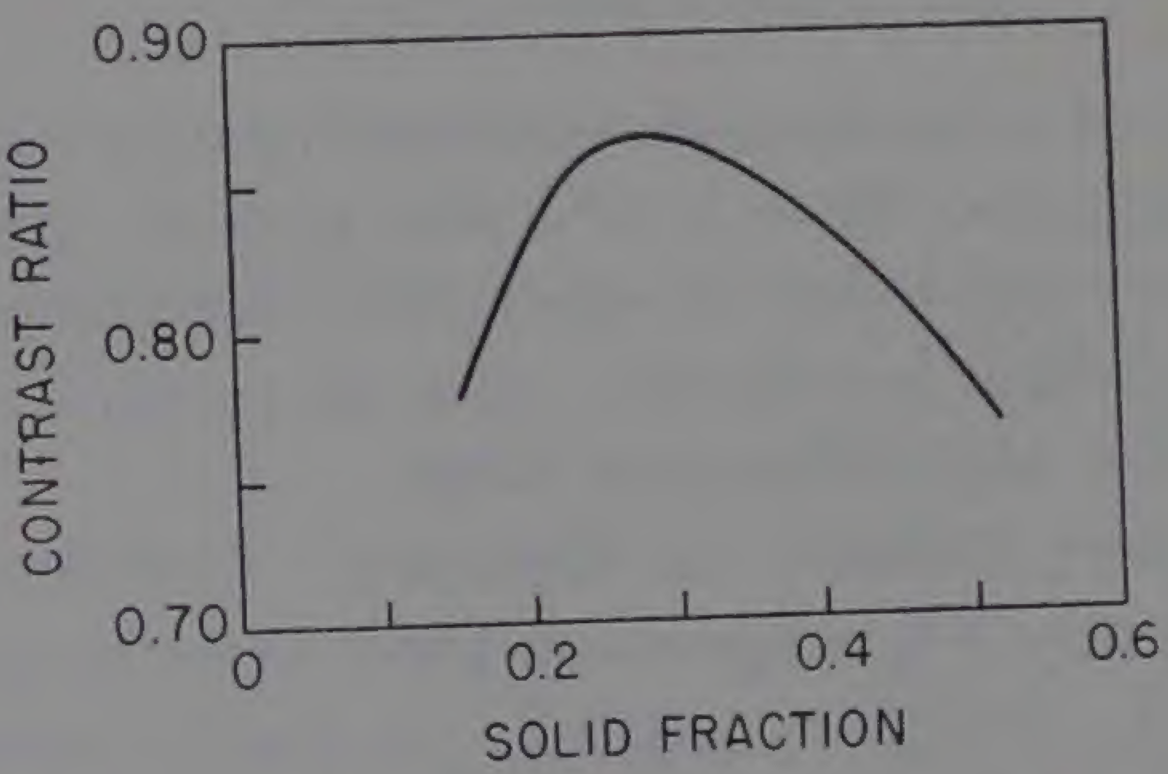

Fig. XVI-29. Effect of solid fraction on opacity. Unbeaten spruce sulfite wet-pressed into sheets. Basis weight 40 lb., 25 × 36—500.

It is obvious from the above that one method of producing a transparent paper is to process the pulp mechanically through beating so that it forms a sheet of high solid fraction which contains a minimum of fiber-air interfaces. Calendering increases the transparency for the same reason. Smoothness of the paper is a factor, since the opacity tends to decrease as the smoothness of the paper is increased.

Effect of Fillers on Opacity. The increase in opacity which results from filling is due to an increase in the scattering coefficient of the paper. In filled paper, the pigment and fiber scatter light independently of each other.[229] Three interfaces are involved: fiber-air, pigment-fiber, and pigment-air.

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[226] J. d'A. Clark, *Pulp Paper Mag. Canada 44,* No. 2:91–102 (Feb., 1943)
[227] R. H. Doughty, *Tech. Assoc. Papers 16:* 406 (June, 1933)
[228] D. B. Wicker, *Paper Trade J. 110,* No. 1:8–14 (Jan. 4, 1940)

Reflection and scattering are greatest at the pigment-air interface. Less scattering occurs at the pigment-fiber interface, e.g., in the case of titanium dioxide, reflection is 18% for perpendicular incidence from air to titanium, and about 6% for perpendicular incidence from cellulose to titanium.[230] There is relatively little scattering at a clay-fiber interface, due to the small difference in the refractive indices of clay and cellulose. In pigment-filled papers most of the surface area of the pigment is not in optical contact with the fibers, and hence most of the scattering occurs at pigment-air interfaces. Anything which increases the number of pigment-fiber interfaces at the expense of pigment-air interfaces will lower the opacity. Increased wet pressing of pigment-filled papers tends to lower the opacity, not only because it increases the amount of fiber bonding, but also because it increases the bonding between the pigment particles and the fibers, thereby substituting pigment-fiber interfaces for pigment-air interfaces.

The scattering coefficients for a number of papermaking pigments are given in the chapter on filling. In choosing a pigment for its opacifying effect, it is wise to choose one with a high scattering coefficient (S value). Pigments with high absorption coefficients (K values) also increase the opacity, but they reduce the brightness. The effectiveness of fillers in increasing opacity depends upon the type of fibrous furnish, as well as the amount of beating given the stock.[231] Certain of the white pigments increase the brightness, as well as increase the opacity of paper. It is possible, by using a combination of a white pigment and a dyestuff, to obtain an exceptionally large increase in opacity by maintaining a constant brightness.[232]

A given amount of pigment used as a filler produces a higher opacity than the same amount of pigment used as a coating.[233] Close packing of pigment particles causes interference which decreases the effectiveness of the particles as reflecting units, thus accounting for the reduced opacity of coated papers, since the pigments in coating are closely packed compared with the pigments in paper.[234]

Mineral constituents left in the paper after the cooking and bleaching operations increase the opacity, although they have a minor effect when

[229] F. A. Steele, *Paper Trade J. 104,* No. 8: 129–130 (Feb. 25, 1937)

[230] L. C. Lewis, *Paper Trade J. 103,* No. 22: 323–330 (Nov. 26, 1936)

[231] H. Gaegauf and M. Muller, *Textil-Rundschau,* No. 6: 222–229; No. 7: 258–265 (1947) through *Bull. Institute Paper Chemistry, 18,* No. 1: 31–32 (1947)

[232] E. R. Laughlin, *Paper Trade J. 111,* No. 22: 275–281 (Nov. 28, 1940)

[233] R. W. Ball and O. P. Lane, *Paper Mill 59,* No. 21: 20–22, 24–25 (May 23, 1936)

[234] R. H. Sawyer, *J. Applied Phys. 13,* No. 10: 596–601 (Oct., 1942)

present in less than 1%.[235] Excess alumina, starch, or other gelatinous materials lower the opacity because they increase the area in optical contact.

Effect of Dyestuffs on Opacity. Dyestuffs have a pronounced effect on opacity. Laughlin[236] found, at least in the range of tinted whites, that the fiber, filler, and dyestuff in the paper each absorb and scatter light independently of the other, and that the opacifying effects are additive. The effect of dyestuffs on opacity is obvious in the case of a thin, deeply dyed black paper which may owe nearly all its opacity to light absorption. The effect is not so obvious in the case of white papers tinted with a small amount of dyestuff, but even this small amount of added dyestuff tends to increase the opacity by absorbing part of the light. Blue-white papers are generally more opaque than yellow-white papers, because the blue-white is obtained by adding blue dye to the pulp. For example, Steele[237] presents the following data for two different papers made from the same pulp:

Test	Blue-white	Creamy white
Reflectivity	0.778	0.824
Opacity (TAPPI)	0.962	0.936

As can be seen, adding blue dye to obtain a blue-white color lowered the brightness, but increased the opacity of the paper. Wicker[238] found that certain dyes have the ability to increase the transparency of glassine, but this is because the dye decreases the diffuse transmittance to a greater degree than the parallel transmittance. The opacifying effect of dyestuffs is less on relatively opaque pulps, such as groundwood, than on rag or sulfite stocks.[239]

When part of the opacity of paper is due to the presence of dyestuffs, the wavelength of the light used for viewing the sample is very important. In general, the maximum opacifying effect of a dyestuff is obtained when the light used for measuring opacity has a wavelength corresponding to the maximum absorption for the dyestuff. In the case of most uncolored papers, the opacity as measured by contrast ratio is greater when measured with light in the blue end of the spectrum, because this is where the maximum light is absorbed. A curve for a typical white paper is shown in Figure XVI-30.[240] The dotted line in the figure is the opacity of the uncolored paper, whereas the solid line represents the opacity of the same sheet colored with a blue dye (methylene blue) and an orange dye. The blue dye has its maximum absorption at 670 millimicrons (red light), and consequently this is where the maximum opacity is obtained. Laughlin[240] found that methylene blue is almost twice as effective in increasing the opacity when the sample is tested in artificial light as it is when tested in ordinary daylight. The wavelength of the viewing light also has a considerable effect on transparency.[241]

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[235] D. B. Wicker, *Paper Trade J. 110,* No. 1: 8–14 (Jan. 4, 1940)
[236] E. R. Laughlin, *Paper Trade J. 111,* No. 22: 275–281 (Nov. 28, 1940)
[237] F. A. Steele, *Paper Trade J. 100,* No. 12: 151–156 (March 21, 1935)
[238] D. B. Wicker, *Paper Trade J. 110,* No. 1: 8–14 (Jan. 4, 1940)
[239] E. R. Laughlin, *Paper Trade J. 111,* No. 22: 275–281 (Nov. 28, 1940)
[240] E. R. Laughlin, *Paper Trade J. 111,* No. 22: 275–281 (Nov. 28, 1940)

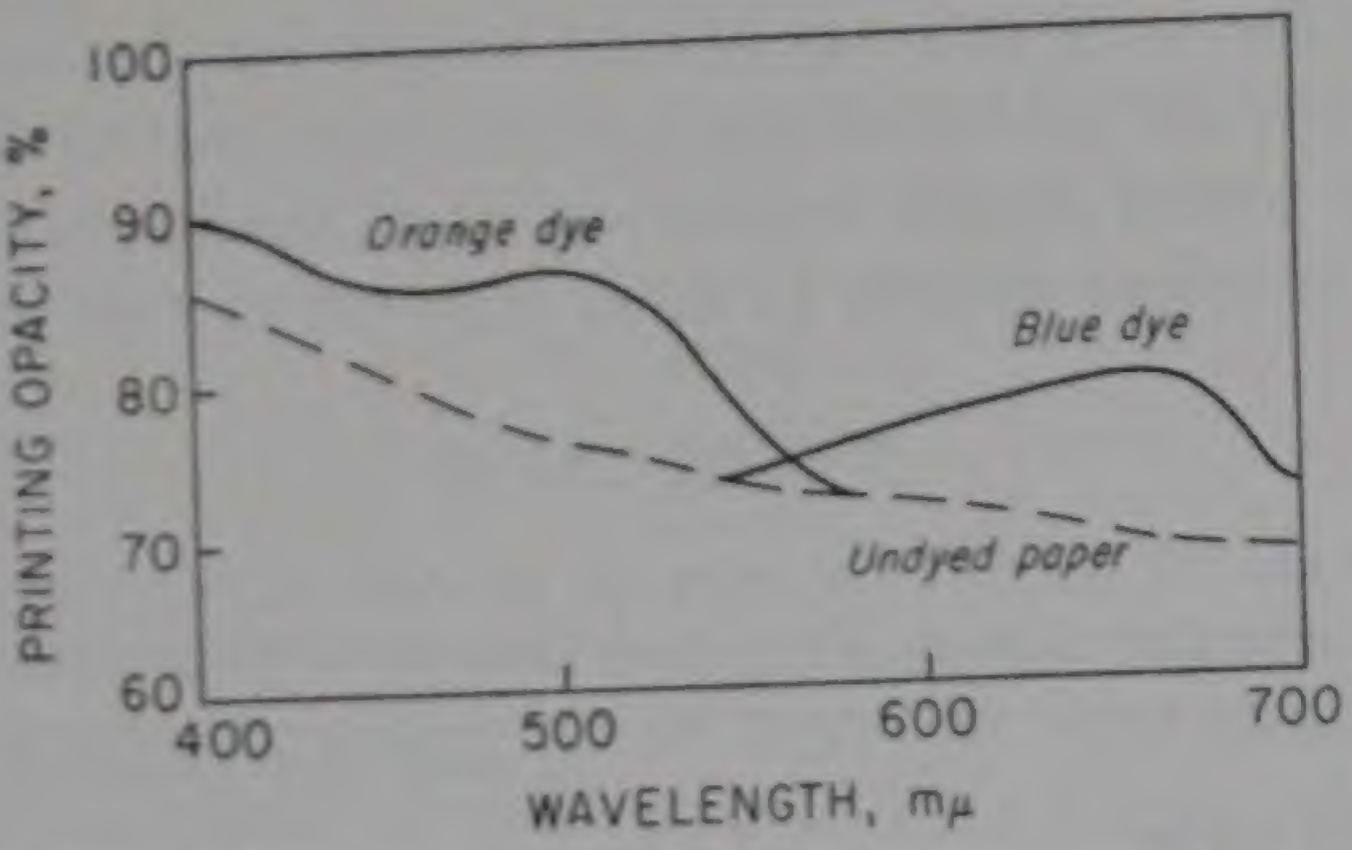

Fig. XVI-30. Effect of dyestuffs on opacity.

Effect of Waxing on Opacity. If paper is impregnated with paraffin or similar material having an index of refraction close to that of cellulose, the opacity of the paper is greatly reduced. Even if the paper is filled or coated with talc, clay, or other pigments having a refractive index in the neighborhood of 1.5, the opacity of the paper will be very low after waxing. On the other hand, if pigments of high refractive index (e.g., zinc sulfide or titanium dioxide) are present in the paper, the paper will retain a high degree of opacity after waxing. Table XXVI shows the amount of light reflected from different air, fiber, titanium dioxide, and wax interfaces, and illustrates the effect of titanium dioxide on the amount of reflected light after waxing.[242]

TABLE XXVI

AMOUNT OF REFLECTION OF LIGHT AT VARIOUS INTERFACES

Interface	Per cent light reflected
Cellulose-air	4.0
Cellulose-wax	0.1
Titanium dioxide-wax	7.5
Titanium dioxide-air	18.0

The effect of waxing on the opacity of two different unfilled papers and the corresponding papers after filling with 5% titanium dioxide is:[243]

Opacity of waxed paper, unfilled	Opacity of waxed paper filled with titanium dioxide
20%	57%
50%	80%

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[241] L. C. Lewis, *Paper Trade J. 103*, No. 22: 323–330 (Nov. 26, 1936)
[242] *Idem.*
[243] *The Handbook*, Titanium Pigment Corporation, National Lead Company, 11 Broadway, New York, N. Y. (1949)

Table XXVII shows the effect of a small amount of titanium dioxide in clay-coated papers on the opacity after waxing. It can be seen from this table that increasing the coat weight from 0 to 8 lb. increased the opacity of the waxed paper from 24.5 to only 29.5% for the clay-coated paper, whereas the same increase in coat weight for the sample containing 10% titanium dioxide increased the opacity from 24.5 to 50.5%. This is the reason why coated papers for waxing (e.g., opaque bread wrap) must be coated with titanium dioxide or other pigment of high refractive index.

TABLE XXVII

EFFECT OF WAXING ON TAPPI OPACITY OF AN ALL CLAY-COATED PAPER AND A CLAY-COATED PAPER CONTAINING TITANIUM DIOXIDE AT DIFFERENT COAT WEIGHTS

Type of coating	Coating weight, pounds 25 × 40—500							
	0		4		6		8	
	U	W	U	W	U	W	U	W
All clay	86.6	24.5	90.1	27.5	91.0	28.0	91.5	29.5
Contg. clay plus 10% TiO_2	86.6	24.5	90.8	39.5	91.8	45.0	92.7	50.5

U, unwaxed. W, waxed.

One interesting point in connection with coated papers is that waxing practically eliminates the effect of the adhesive. In other words, although the amount of adhesive used in the coating before waxing has a pronounced effect on the opacity, once the sheet is waxed, the adhesive ratio is no longer a significant factor because the refractive indices of the adhesive and wax are very close to each other.

Effect of Different Pulps on Opacity. For paper made from a given pulp, the opacity is a direct function of the fineness of the fibers, that is, the fiber diameter. The length of the fibers has little or no effect on opacity,[244] since fiber length does not affect the number of transverse fiber-air interfaces, due to the fact that nearly all fibers lie in the plane of the sheet and light passes through them only transversely. Short-fibered pulps such as hardwood soda and groundwood tend to produce papers of relatively high opacity, but this is due, in the case of soda pulp, to the relatively poor bonding qualities and, in the case of groundwood, to the poor color. The same hardwood species cooked by the sulfite process instead of the soda process produce papers of low opacity because of the high degree of fiber bonding and the high sheet density.[245]

The effect of fiber size on the specific surface and opacity of groundwood pulps is shown in Table XXVIII, taken from work by Parsons.[245] These results show that the specific surface and the opacifying effect in-

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[244] L. C. Lewis, *Paper Trade J. 103,* No. 22: 323–330 (Nov. 26, 1936)

[245] S. R. Parsons, *Paper Trade J. 115,* No. 25: 314–322 (Dec. 17, 1942)

TABLE XXVIII

Effect of Fiber Size on Specific Surface and Opacifying Effect of Groundwood Pulp

Fraction	Specific surface, sq.cm./g. (silvering technique)	Printing opactiy, R_0/R_∞, %
12–20	11,400	79.8
12–35	12,500	85.0
12–65	13,900	87.4
12–150	24,100	91.1
12–fines	47,400	98.8
12–0	34,200	92.6

crease as the fiber dimensions are decreased. The fines have a disproportionately high opacifying effect, due to their high light absorption.

Because of their inherent light absorption and light scattering powers, each major grade of pulp has a rather consistent or typical effect on the opacity. However, the opacity obtainable with any pulp depends upon the amount of beating and calendering, and also on other papermaking factors which affect the degree of bonding in the sheet. Hence, any listing of pulps according to their opacifying effect is only relative. However, it may be stated as a general rule that the opacity of paper is higher the lower the reflectivity of the pulp from which the paper is made. Thus, unbleached pulps produce papers of higher opacity than bleached pulps, due to the fact

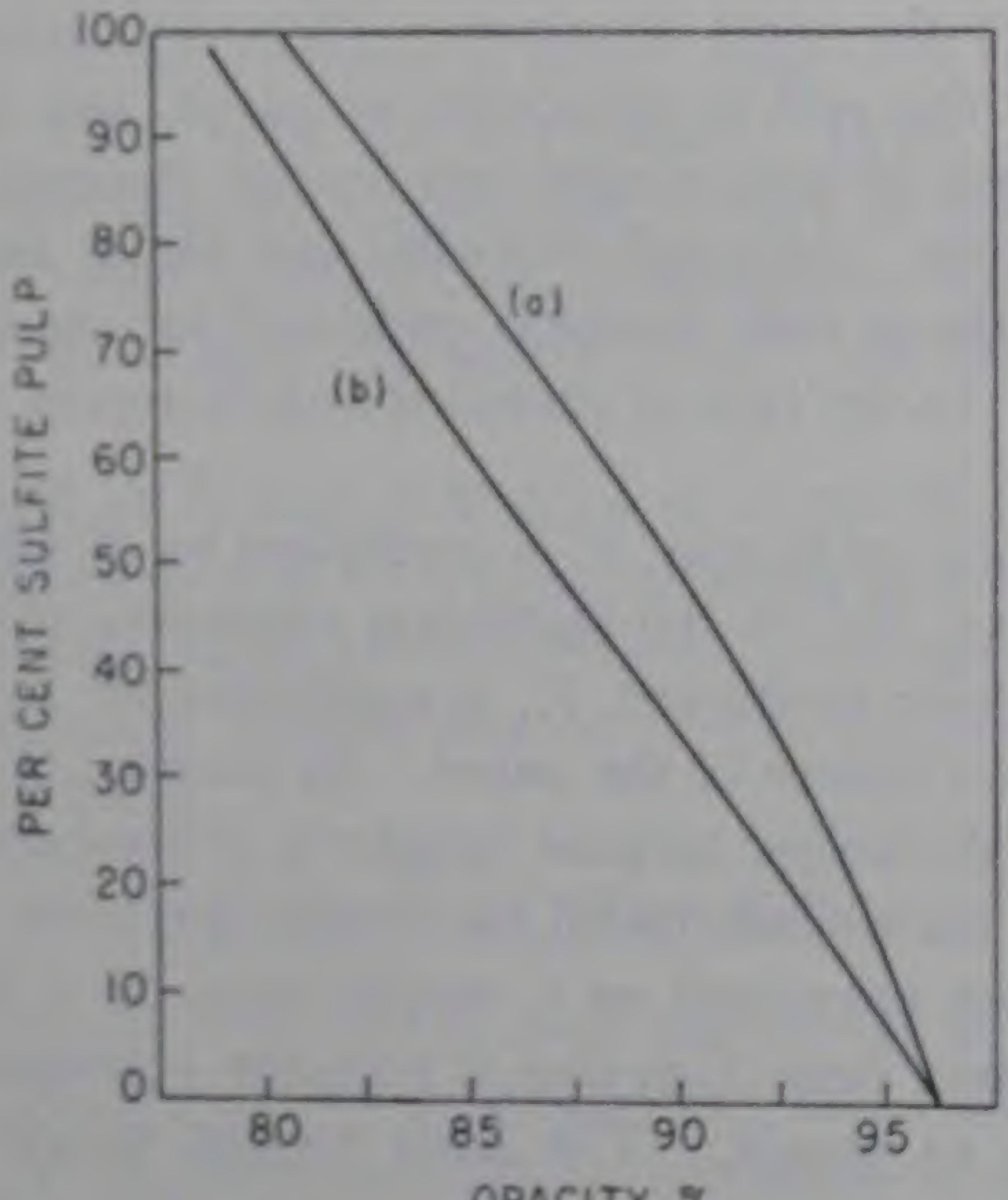

Fig. XVI-31. Effect of unbleached (a) and bleached (b) sulfite pulp—both with groundwood—on the opacity of newsprint.

that lignin absorbs more light than cellulose. The effect of adding different amounts of unbleached and bleached sulfite pulps to a groundwood furnish is shown in Figure XVI-31. Maass[246] points out that the addition of a little unbleached sulfite to a groundwood furnish has relatively little effect on the transmittance or reflectance of light, compared with the significant decrease in transmittance and increase in reflectance obtained when a little groundwood is added to an unbleached sulfite furnish.

Kubelka and Munk Theory

The theory of Kubelka and Munk has been extremely helpful in understanding the optical properties of paper. This theory is based on the definition of two fundamental optical constants: the specific scattering coefficient (S) and the specific absorption coefficient (K). These coefficients are characteristic of any diffusing material such as paper and are defined[247] as follows: (*1*) K is the limiting value of the absorption of light energy per unit thickness as the thickness becomes very small; (*2*) S is the limiting value of light energy scattered backwards per unit of thickness as the thickness becomes very small. The K value is proportional to the average length of path traversed by the light in passing through the material, is inversely proportional to the density, and is a function of the refractive index; it is determined by the chemical nature of the paper. The S value is proportional to the total surface area per unit mass of the material, inversely proportional to the density, and increases with the refraction index;[247] it is mostly a matter of the sheet structure. These fundamental constants, K and S, determine the optical properties of paper, and are very useful in calculating the effect of basis weight and furnish changes on the reflectance and opacity of paper. Although Kubelka and Munk theory holds strictly for homogeneous sheets only, it works quite well for sheets containing up to about 10% filler. In the case of coated sheets, however, it may lead to appreciable error.[248]

If the scattering coefficient, S, is multiplied by X (the thickness of the paper), the product, SX, is the scattering coefficient of the paper. Likewise, if the absorption coefficient, K, is multiplied by X, the product, KX, is the absorption coefficient of the paper. In practice, X is represented by weight instead of thickness, because weight is a common unit of specification, and because coefficients based on weight are more easily handled in calculations. When expressed on a weight basis, S^1 is sometimes used as the symbol; it differs from S in that it contains a proportionality constant relating thickness to weight. The basis weight should be expressed in terms of the standard ream 25 × 40—500. S and S^1 are not fundamentally the same quantity. For example, if a sample of paper is compressed in the dry condition, the S^1 and S^1X values are not greatly affected, but the S value increases because of the greater number of scattering particles per unit of thickness. The S^1 value is a characteristic of the material in the paper, and is not influenced by the weight or thickness of the paper, although it is influenced by physical changes in the material making up the paper. For example, beating affects the S^1 value of pulp, and particle size affects the S^1 value of a pigment. Unless otherwise stated, the S values reported in the following discussion are based on weight rather than on thickness and are in reality S^1 values.

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[246] O. Maass, *Pulp Paper Mag. Canada 37*: 689–695 (Nov. 1936)

[247] M. N. Davis. *Paper Trade J. 111*, No. 14: 184–188 (Oct. 3, 1940)

[248] Institute of Paper Chemistry, Instrumentation Studies, *Paper Trade J. 109*, No. 4: 31–36 (July 27, 1939)

Kubelka and Munk Equation. The Kubelka and Munk equation may be expressed as follows for diffuse light:

$$R_\infty = 1 + (K/S) - [(K/S)^2 + 2(K/S)]^{0.5}$$

where K is the absorption coefficient, S is the scattering coefficient, and R_∞ is the reflectance of a pad thick enough to be opaque. If made at the proper wavelength, the R_∞ value is papermaker's brightness. The derivation of this formula has been shown by Steele and Judd.[249, 250]

The above equation may be transformed into a more workable form as shown below:

$$K/S = [1 - R_\infty]^2/2R_\infty$$

By the use of this simple formula, a single brightness reading (R_∞) will serve to give the K/S value for any paper. Table XXIX shows the relationship between monochromatic reflectance of an opaque pad of paper (R_∞) and the K/S value of the paper. It should be stressed that a single measurement of R_∞ gives only the ratio of K to S, not the individual K and S values.

Determination of *K* and *S* Values of Pulp Mixtures. For most practical purposes, the K/S of a pulp mixture can be determined from the K/S values of the components of the mixture. This can be done by means of the following relation, without having to find the individual K and S values of each component.

$$(K/S)_{\text{mixture}} = C_1(K/S)_1 + C_2(K/S)_2$$

where C_1 and C_2 are the fractions of each component of the pulp mixture, and $(K/S)_1$ and $(K/S)_2$ are the corresponding values for each component.

Although the above formula is not fundamentally correct, it works very well in practice, provided the components are of the same order of magnitude. All that is necessary to use the above relationship is to obtain the

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[249] D. B. Judd, *Paper Trade J. 106,* No. 1: 5–12 (Jan. 6, 1938)
[250] F. A. Steele, *Paper Trade J. 100,* No. 12: 151–156 (March 21, 1935)

TABLE XXIX

RELATION BETWEEN K/S AND R_∞

R_∞	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	∞	449.000	249.000	165.668	124.002	99.002	82.336	70.432	61.504	54.561
1	49.005	44.460	40.673	37.468	34.720	32.341	30.258	28.420	26.787	25.325
2	24.010	22.820	21.738	20.751	19.845	19.012	18.244	17.532	16.871	16.256
3	15.682	15.145	14.641	14.168	13.723	13.303	12.907	12.532	12.177	11.840
4	11.520	11.216	10.926	10.649	10.386	10.134	9.893	9.662	9.441	9.229
5	9.025	8.829	8.641	8.460	8.286	8.118	7.957	7.800	7.650	7.513
6	7.363	7.227	7.096	6.968	6.844	6.725	6.609	6.496	6.387	6.281
7	6.178	6.078	5.980	5.886	5.794	5.704	5.617	5.532	5.449	5.369
8	5.290	5.213	5.139	5.066	4.994	4.925	4.857	4.791	4.726	4.662
9	4.601	4.540	4.481	4.423	4.366	4.311	4.256	4.203	4.151	4.100
10	4.050	4.001	3.953	3.906	3.860	3.814	3.770	3.718	3.684	3.642
11	3.600	3.560	3.520	3.481	3.493	3.405	3.368	3.332	3.296	3.261
12	3.227	3.193	3.159	3.127	3.094	3.062	3.031	3.001	2.970	2.940
13	2.911	2.882	2.854	2.826	2.798	2.771	2.744	2.718	2.692	2.667
14	2.641	2.617	2.592	2.568	2.544	2.521	2.498	2.475	2.452	2.430
15	2.408	2.387	2.365	2.344	2.324	2.303	2.283	2.263	2.244	2.224
16	2.205	2.186	2.167	2.149	2.131	2.113	2.095	2.078	2.060	2.043
17	2.026	2.009	1.993	1.977	1.961	1.945	1.929	1.913	1.898	1.883
18	1.868	1.853	1.838	1.824	1.809	1.795	1.781	1.767	1.754	1.740
19	1.727	1.713	1.700	1.687	1.674	1.662	1.649	1.637	1.624	1.612
20	1.600	1.588	1.576	1.565	1.553	1.542	1.530	1.519	1.508	1.497
21	1.486	1.475	1.464	1.454	1.443	1.433	1.423	1.413	1.403	1.393
22	1.383	1.373	1.363	1.354	1.344	1.335	1.325	1.316	1.307	1.298
23	1.289	1.280	1.271	1.262	1.254	1.245	1.237	1.228	1.220	1.212
24	1.203	1.195	1.187	1.179	1.171	1.163	1.156	1.148	1.140	1.133
25	1.125	1.118	1.110	1.103	1.095	1.088	1.081	1.074	1.067	1.060

R_∞	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
26	1.053	1.046	1.039	1.033	1.026	1.019	1.013	1.006	0.997	0.993
27	0.987	0.981	0.974	0.968	0.962	0.956	0.950	0.944	.938	.932
28	.926	.920	.914	.908	.903	.897	.891	.886	.880	.875
29	.869	.864	.858	.853	.848	.842	.837	.832	.827	.822
30	.817	.812	.807	.802	.797	.792	.787	.782	.777	.773
31	.768	.763	.759	.754	.749	.745	7.40	.736	.731	.727
32	.722	.718	.714	.709	.705	.701	.697	.693	.688	.684
33	.680	.676	.672	.668	.664	.660	.656	.652	.648	.644
34	.641	.637	.633	.629	.625	.622	.618	.614	.611	.607
35	.604	.600	.596	.593	.589	.586	.582	.579	.576	.572
36	.569	.566	.562	.559	.556	.552	.549	.546	.543	.540
37	.536	.533	.530	.527	.524	.521	.518	.515	.512	.509
38	.506	.503	.500	.497	.494	.491	.488	.485	.483	.480
39	.477	.474	.472	.469	.466	.463	.461	.458	.455	.453
40	.450	.447	.445	.442	.440	.437	.435	.432	.429	.427
41	.425	.422	.420	.417	.415	.412	.410	.408	.405	.403
42	.400	.398	.396	.394	.391	.389	.387	.384	.382	.380
43	.378	.376	.373	.371	.369	.367	.365	.363	.361	.358
44	.356	.354	.352	.350	.348	.346	.344	.342	.340	.338
45	.336	.334	.332	.330	.328	.326	.324	.323	.321	.319
46	.317	.315	.313	.311	.310	.308	.306	.304	.302	.301
47	.299	.297	.295	.294	.292	.290	.288	.287	.285	.283
48	.282	.280	.278	.277	.275	.273	.272	.270	.269	.267
49	.265	.264	.262	.261	.259	.258	.256	.255	.253	.251
50	.250	.248	.247	.246	.244	.243	.241	.240	.238	.237
51	.235	.234	.233	.231	.230	.228	.227	.226	.224	.223
52	.222	.220	.219	.218	.216	.215	.214	.212	.211	.210
53	.208	.207	.206	.205	.203	.202	.201	.200	.198	.197

Table continued

TABLE XXIX (*continued*)

R_∞	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
54	.196	.195	.194	.192	.191	.190	.189	.188	.186	.185
55	.184	.183	.182	.181	.180	.178	.177	.176	.175	.174
56	.173	.172	.171	.170	.169	.167	.166	.165	.164	.163
57	.162	.161	.160	.159	.158	.157	.156	.155	.154	.153
58	.152	.151	.150	.149	.148	.147	.146	.145	.144	.143
59	.14246	.142	.141	.13967	.13875	.13784	.13693	.13602	.13512	.13422
60	.13333	.13245	.13156	.13069	.12981	.12895	.12808	.12722	.12637	.12552
61	.12467	.12383	.12299	.12216	.12133	.12051	.11969	.11887	.11806	.11725
62	.11645	.11565	.11486	.11407	.11328	.11250	.11172	.11095	.11018	.10941
63	.10865	.10789	.10714	.10639	.10564	.10490	.10416	.10343	.10270	.10197
64	.10125	.10053	.09982	.09910	.09840	.09769	.09699	.09630	.09560	.09492
65	.09423	.09355	.09287	.09220	.09153	.09086	.09020	.08954	.08888	.08823
66	.08758	.08693	.08629	.08565	.08501	.08438	.08375	.08313	.08250	.08188
67	.08127	.08066	.08005	.07944	.07884	.07824	.07764	.07705	.07646	.07588
68	.07529	.07471	.07414	.07356	.07299	.07243	.07186	.07130	.07074	.07019
69	.06964	.06909	.06854	.06800	.06746	.06692	.06639	.06586	.06533	.06481
70	.06429	.06377	.06325	.06274	.06223	.06172	.06122	.06071	.06021	.05972
71	.05923	.05873	.05825	.05776	.05728	.05680	.05632	.05585	.05538	.05491
72	.05444	.05398	.05352	.05306	.05261	.05216	.05171	.05126	.05081	.05037
73	.04993	.04949	.04906	.04863	.04820	.04777	.04735	.04693	.04651	.04609
74	.04568	.04526	.04485	.04445	.04404	.04364	.04324	.04284	.04245	.04206
75	.04167	.04128	.04089	.04051	.04013	.03975	.03938	.03900	.03863	.03826
76	.03789	.03753	.03717	.03681	.03645	.03609	.03574	.03539	.03504	.03470
77	.03435	.03401	.03367	.03333	.03299	.03266	.03233	.03200	.03167	.03135
78	.03103	.03070	.03039	.03007	.02976	.02944	.02913	.02882	.02852	.02821
79	.02791	.02761	.02731	.02702	.02672	.02643	.02614	.02585	.02557	.02528
80	.02500	.02472	.02444	.02417	.02389	.02362	.02335	.02308	.02281	.02255
81	.02228	.02202	.02176	.02151	.02125	.02100	.02075	.02050	.02025	.02000

R_∞	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
82	.01976	.01951	.01927	.01903	.01880	.01856	.01833	.01809	.01786	.01764
83	.01741	.01718	.01696	.01674	.01652	.01630	.01609	.01587	.01566	.01545
84	.01524	.01503	.01482	.01462	.01442	.01422	.01402	.01382	.01362	.01343
85	.01324	.01304	.01285	.01267	.01248	.01230	.01211	.01193	.01175	.01157
86	.01140	.01122	.01105	.01087	.01070	.01054	.01036	.01020	.01004	.00987
87	.00971	.00955	.00939	.00924	.00908	.00893	.00878	.00863	.00848	.00833
88	.00818	.00804	.00789	.00775	.00759	.00747	.00733	.00720	.00706	.00693
89	.00680	.00667	.00654	.00641	.00628	.00616	.00604	.00591	.00579	.00567
90	.00555	.00544	.00532	.00521	.00510	.00499	.00488	.00477	.00466	.00456
91	.00445	.00435	.00425	.00415	.00405	.00395	.00385	.00376	.00366	.00357
92	.00348	.00339	.00330	.00321	.00313	.00304	.00296	.00287	.00279	.00271
93	.00263	.00256	.00248	.00241	.00233	.00226	.00219	.00212	.00205	.00198
94	.00191	.00185	.00179	.00172	.00166	.00160	.00154	.00148	.00143	.00137
95	.00132	.00126	.00121	.00116	.00111	.00106	.00101	.00097	.00092	.00088
96	.00083	.00079	.00075	.00071	.00067	.00063	.00060	.00056	.00053	.00050
97	.00046	.00043	.00040	.00037	.00035	.00032	.00030	.00027	.00025	.00023
98	.00020	.00018	.00016	.00015	.00013	.00011	.00010	.00009	.00007	.00006
99	.00005	.00004	.00003	.00002	.00002	.00001	.00001	.00000	.00000	.00000
100.0	00000									

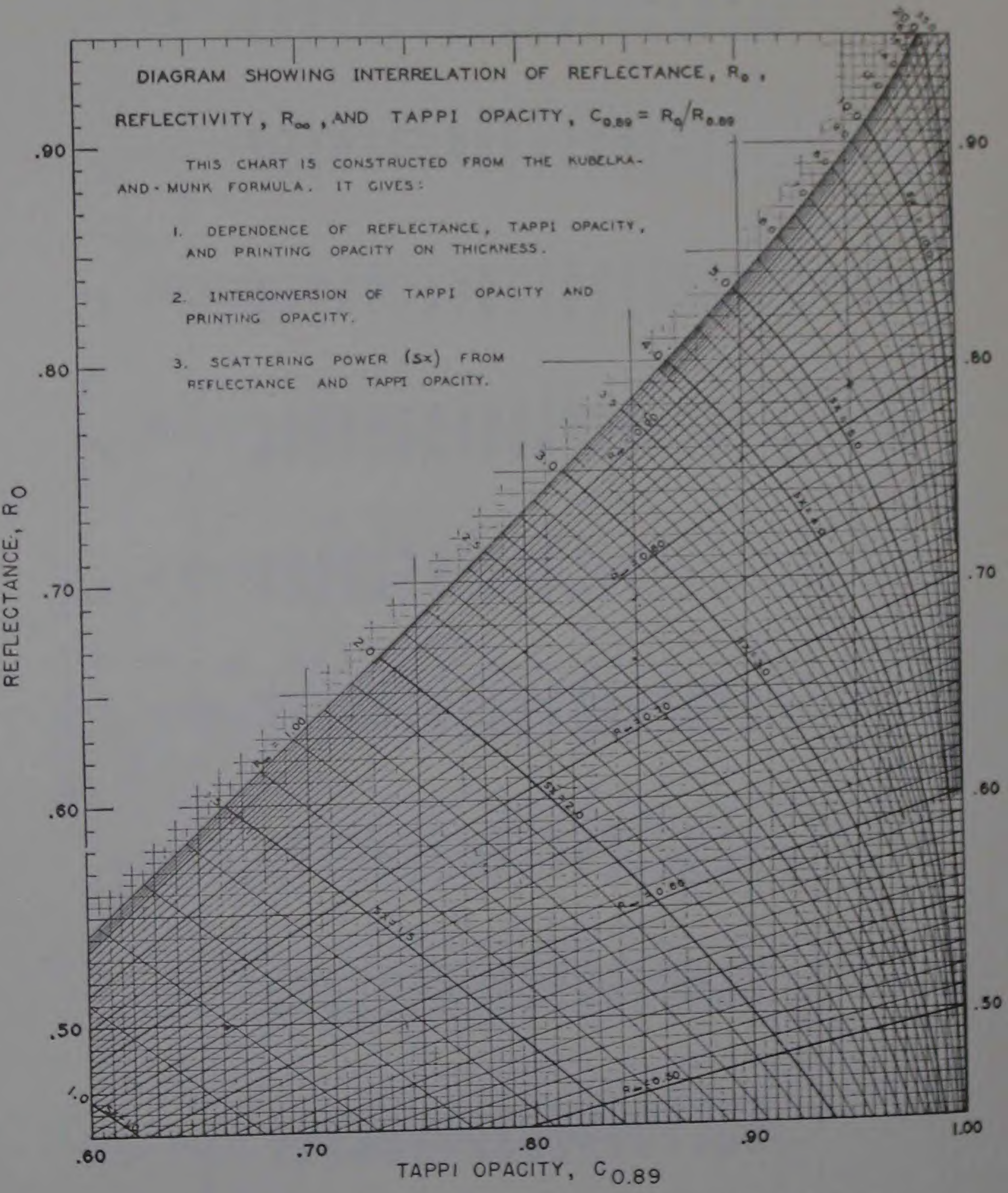

Fig. XVI-32. Relation between reflectance over black backing, TAPPI opacity, reflectivity, and scattering power *SX* (courtesy *National Bureau of Standards*).

K/S value of each component of the pulp mixture from the brightness (R_∞) reading by using Table XXIX, and then to substitute in the formula.

In the case of mixtures where there is a marked difference in K/S values of the different components, the above relationship cannot be used because it is necessary to use individual K and S values. Once the individual K and S values are known, the following relationship can be used:

$$\frac{K_{1,2}}{S_{1,2}} = \frac{C_1K_1 + C_2K_2}{C_1S_1 + C_2S_2}$$

where C_1 is the part by weight of material 1, and C_2 is the part by weight of material 2.

To determine K and S values individually, a reflectance measurement $R_{R'}$ of a known thickness, X, over a background of reflectance R^1 is necessary in addition to the R_∞ reading. The following relation can then be used.

$$SX = \frac{2.303}{1/R_\infty - R_\infty} \log \frac{[R_{0.98} - (1/R_\infty)]\,[0.98 - R_\infty]}{[0.98 - (1/R_\infty)]\,[R_{0.98} - R_\infty]}$$

S is found, from the above relationship, by dividing SX by X; K is found by multiplying the K/S value (obtained as described above) by S.

The calculation of SX from the above formula is obviously quite complicated. In order to simplify calculation, Kubelka[252] has given a set of formulas in terms of hyperbolic functions by which exact calculations of SX can be made conveniently. It is also possible to make rapid, approximate graphical solution by use of the curves in Figure XVI-32, which show the interrelationships between reflectivity (R_∞), reflection (R_0), TAPPI opacity ($R_0/R_{0.89}$), printing opacity (R_0/R_∞), and scattering power SX. Two families of curves are plotted on a single set of coordinates, the ordinate being R_0 and the abscissa being TAPPI opacity ($C_{0.89} = R_\infty/R_{0.89}$). By the use of these curves, a reading of SX can be obtained from a knowledge of the TAPPI opacity ($C_{0.89}$) and the reflectivity (R_∞). Thus, S values can be determined from this chart, if the basis weight 25 × 40—500 (X) is known, by dividing SX by X. Knowing the S value and the reflectivity (R_∞), the K value can then be determined from Table XXIX.

Factors Affecting *K* and *S* Values of Pulp. Once the K and S values have been determined for a given pulp, it can be assumed that these values of the pulp remain constant, unless changes are made in the method of pulp preparation or a new pulp is used. Steele[253] gives comparative S values for different pulps, as shown in Table XXX, when the pulps are treated in the same way. These values are based on a basis weight of 17 × 22—500. These are only comparative values, of course, and should not be taken as absolute values.

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[252] P. Kubelka, *J. Optical Soc. America 38:* 448–458 (1948)

[253] F. A. Steele, *Paper Trade J. 100,* No. 12: 151–156 (March 31, 1935)

TABLE XXX

COMPARATIVE S VALUES FOR SEVERAL DIFFERENT PULPS

Type of pulp	S value (17 × 22—500)
Unbleached sulfite	0.086–0.111
Bleached sulfite	0.106–0.133
Soda pulp	0.174
Bleached kraft	0.186

Judd[254] has presented data demonstrating how the scattering coefficients of paper can be determined from measurements of conventional optical properties. The results obtained on four different commercial papers, rag writing, sulfite writing, book, and newsprint, are shown in Table XXXI. The R_0 and $C_{0.89}$ values were obtained experimentally, and R_∞ and SX values determined from curves similar to Fig. XVI-32. Coefficient of scatter per inch and coefficient of scatter per pound were obtained by dividing the SX values respectively by the thickness of the paper (in inches) and basis weight of the paper (in pounds 25 × 40—500).

TABLE XXXI

CALCULATION OF COEFFICIENT OF SCATTER FROM R_0 AND $C_{0.89}$

Data	Rag writing	Sulfite writing	Book	Newsprint
Paper thickness X, in.	0.0028	0.0037	0.0048	0.0056
Basis wt. of paper X, lb. (25 × 40—500)	38	52	62.5	53
Ash, %	0.36	0.34	5.82	0.38
R_0	0.683	0.677	0.785	0.605
$C_{0.89} = R_0/R_{0.89}$	0.767	0.807	0.937	0.985
R_∞ from chart	0.890	0.805	0.827	0.609
SX from chart	2.23	2.40	5.05	4.28
Coeff. of scatter S, per in.	800	650	1050	760
Coeff. of scatter S^1, per lb. (25 × 40—500)	0.059	0.046	0.081	0.081

Book and newsprint have a high scattering coefficient, as can be seen from Table XXXI. The high S value of book paper can be ascribed to the presence of filler (high ash). The high S value for newsprint can be ascribed to the presence of darkly colored groundwood. It can be seen from the results in the table that book paper has about the same S value as newsprint when S is expressed on a weight basis, but that the S value of book paper is much larger than that of newsprint when the S value is expressed on the basis of thickness.[255] The book paper has a much higher brightness than the newsprint; the S values (weight basis) of the two papers are the same, but the K value of the book paper is lower and consequently the K/S value is lower.

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[254] D. B. Judd, *Paper Trade J. 106,* No. 1: 5–12 (Jan. 6, 1938)

[255] *Idem.*

The specific scattering coefficient of pulp is a linear function of the surface area. Because the surface area is reduced by fiber bonding, it would be expected that anything which increases fiber bonding, such as increased beating or wet pressing, would in turn reduce the S value of the pulp. The effect of beating on the S and K values of a bleached spruce sulfite pulp is shown in Table XXXII.[256] It can be seen from this table that substantial decreases in S occur as a result of beating; the K values showed an initial decrease, followed by an increase, so that the over-all change was small. Nordman[257] has shown that the ratio of the scattering coefficient to the specific surface varies with the type of beating apparatus; a special disintegrator and Clark kollergang, for example, produced pulps having a higher scattering coefficient than a Lampen mill for a particular specific external surface. The loss in scattering coefficient with beating also varies with the type of pulp; for example, bleached sulfite loses scattering power more rapidly than strong sulfite.[258] There are particular cases where beating actually increases the scattering coefficient, but this occurs only if the pulps are formed into paper under conditions where fiber bonding is negligible. For example, increased beating increases the scattering coefficient of pure alpha pulps, and increased beating increases the scattering coefficient of ordinary pulps if the sheets are formed in non-polar liquids.[259]

TABLE XXXII

EFFECT OF BEATING ON K AND S VALUES OF BLEACHED SPRUCE SULFITE PULP

Beating interval (Lampen mill), min.	0	15	30	60
Freeness (S-R), cc.	835	690	520	355
R_∞	0.886	0.882	0.851	0.835
S^1 $(25 \times 40—500)$	0.0537	0.0348	0.0298	0.0249
K^1 $(25 \times 40—500)$	0.0394	0.0275	0.0389	0.0406

The effect of wavelength of light on the S and K values and reflectivity (R_∞) are shown in Table XXXIII for spruce sulfite pulp.[260] The variation in K value and R_∞ with wavelength is to be expected because of the slightly yellowish color of the pulp. The decrease in specific scattering coefficient with increasing wavelength is fairly small and can be attributed to variation in the internal scattering within the fiber with changes in wavelength.

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[256] S. R. Parsons, *Paper Trade J. 115,* No. 25: 314–322 (Dec. 17, 1942)

[257] L. Nordman, *Svensk-Papperstidn. 52,* No. 18: 441–447 (Sept. 30, 1949)

[258] *Idem.*

[259] *Idem.*

[260] S. R. Parsons, *Paper Trade J. 115,* No. 25: 314–322 (Dec. 17, 1942)

TABLE XXXIII

Variation in R_∞, S, and K Values with Wavelength (Spruce Sulfite Pulp)

Wavelength, mμ	R_∞	S, 25 × 40—500	K, 25 × 40—500
420	0.808	0.0659	0.1505
500	0.877	0.0612	0.0528
600	0.899	0.0582	0.0330
700	0.889	0.0548	0.0379

Calculation of Brightness of Pulp Mixtures from *K* and *S* Values. Since the brightness of paper is a function only of the K and S values of the individual components of the paper, it is possible to calculate the brightness of paper made from mixed pulps if the K and S values of the individual pulps are known. The S value for the paper can be calculated by the following formula:

$$SX = S_1{}^1W_1 + S_2{}^1W_2 + S_3{}^1W_3 + \cdots$$

where SX is the scattering power of the paper and the S and W values are the scattering coefficients and weights per reams, respectively, of the various constituents. The K value of the paper may be obtained in the same way, and the ratio K/S obtained by dividing K by S. From this, R_∞ can be obtained by means of Table XXIX. The brightness values calculated in this way agree very closely with experimental brightness values (see Fig. XVI-27).

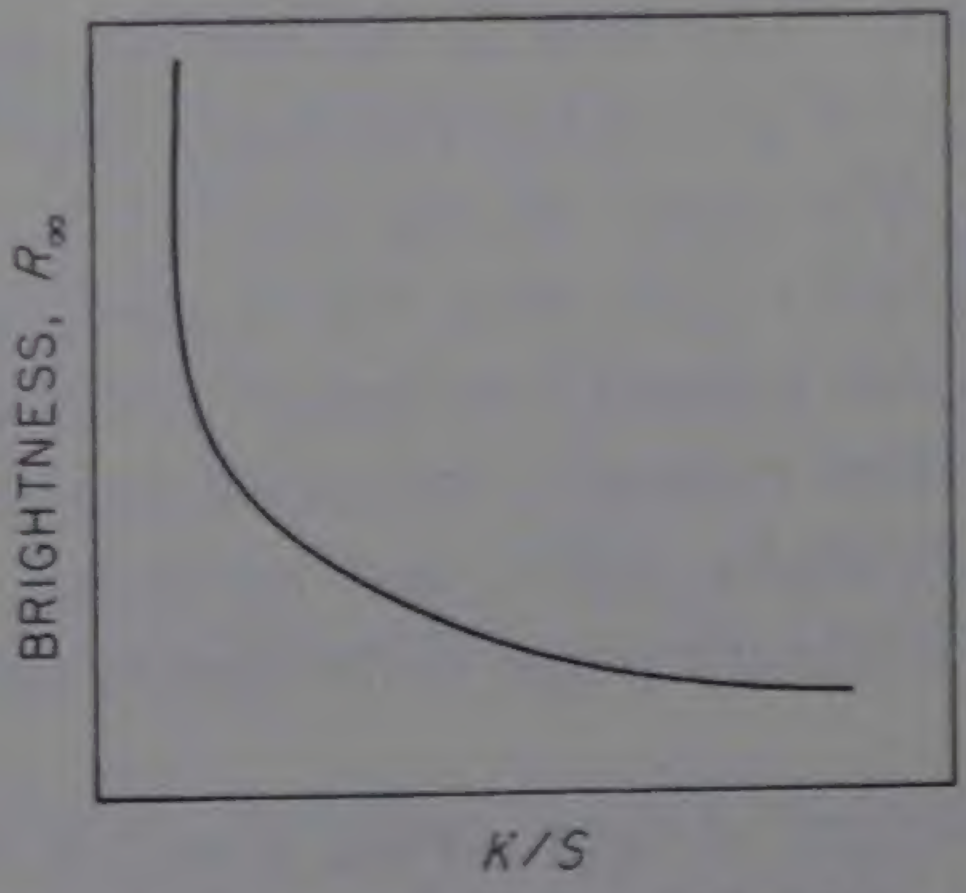

Fig. XVI-33. Variation in brightness with changes in K/S value.

If the reflectivity (R_∞) of paper is plotted against K/S value, a curve of the general shape, shown in Figure XVI-33, is obtained. This figure shows that the reflectance (brightness) falls off rapidly in the range of high R_∞ values for small increases in the K/S value of added material. This illustrates what every practical papermaker knows—that the addition of a small amount of colored material (i.e., high K value) to a bright pulp sharply decreases the brightness. On the other hand, addition of the same material to a dull pulp will have much less dulling effect.

Determination of S Values of Pigments. The S value of pigment in paper can be determined from the S value of the unfilled paper and the S value of the paper after filling with the pigment. For example, consider an unfilled paper of basis weight 20 lb. which has a contrast ratio ($C_{0.89}$) of 0.80 and a reflectivity (R_∞) of 0.84. The SX value of the paper obtained from the curves in Figure XVI-32 is 2.45, and since the basis weight is 20 lb., the S value is 2.45/20 or 0.122. Assuming that a sheet of the same weight made from the same pulp containing 10% filler has a contrast ratio ($C_{0.89}$) of 0.87 and a reflectivity (R_∞) of 0.86, the new SX value of the paper obtained from the curves in Figure XVI-32 is now 3.55, and since the basis weight is the same (20 lb.), the S value of the filled paper is 3.55/20 or 0.178. The S value of the pigment is then determined from the S value of the filled paper, the S value of the unfilled paper, and the proportion of filler (0.10) in the paper as follows:

$$S_{\text{pigment}} = \frac{S_{\text{filled paper}}(0.178) - (1.00 - 0.10)\,S_{\text{unfilled paper}}(0.122)}{0.10}$$

$$S_{\text{pigment}} = 0.69$$

When the S value of a pigment has been determined, it can be used in the same way as the S value of pulp to calculate the S value of paper containing the pigment. The following relationship can be used where P represents the pigment content on a fractional basis:

$$S_{\text{paper}} = (1-P)S_{\text{pulp}} + PS_{\text{pigment}}$$

This relationship works fairly well up to 5 to 10% filler, but unfortunately scattering is not directly proportional to the pigment content of the paper. Consequently, it is desirable to plot a curve of S value of the pigment versus pigment content of the paper for use as a reference.

The S value of a pigment is a measure of its effectiveness in scattering light. The S value is not constant, but varies according to the conditions of use of the pigment. Thus, S value serves as a measure of the effectiveness of a pigment under the particular conditions of use. By studying the effect of manufacturing conditions on the S value of the pigment, it is possible to determine whether the pigment is giving the results it should. Typical S values of different pigments are given in Chapter IX.

Effect of Dyestuffs on K/S Values. Several attempts have been made to study the effect of dyestuffs on the K and S values of paper. Foote[261] found, in the case of a single dyestuff, that the scattering coefficient (S) is practically independent of the amount of dyestuff in the paper for dyeings up to 1 lb. of dyestuff per 1,000 lb. of stock, but that the S value decreases appreciably for heavier dyeings. The absorption coefficient (K) is approximately proportional to the concentration of dye in the range up

[261] W. J. Foote, *Paper Trade J. 109,* No. 25: 333–340 (Dec. 21, 1939)

to 3 lb. of dye per 1,000 lb. of stock. In light tints, he found that the ratio K/S, as determined for the dye alone, is approximately proportional to the dye concentration; in light to medium shades, he found a straight-line relationship between the log K/S and the log concentration of dye, but in medium-deep to full shades, no direct relationship was found. These results are applicable to sheets containing a single dyestuff only. The amount of light reflected by a sheet containing a mixture of dyestuffs cannot be specified by addition, since the amount of light reflected is determined by subtraction.

Nolan[262] used the Kubelka and Munk theory to calculate the reflectivity (brightness) of paper containing two or more dyes by using the K/S value of the undyed pulp and the K/S values of the pulps containing each individual dye. He obtained good agreement between experimental and theoretical spectral reflectivities of handsheets of unbleached sulfite when colored with mixtures of two basic dyes. These results can only be obtained, however, if there is no reaction between the dyes, and if the scattering coefficient of the dyed paper is independent of the concentration of dye.

The effect of dyestuffs on opacity can be calculated by assuming that the dyestuff has no effect on the S value of the paper. When this assumption is made, the effect of dyestuffs on the K value can be calculated if R_∞ is known. The curves in Figure XVI-32 may be used to quickly determine the effect of dyestuffs on opacity. For example, supposing a paper has a reflectivity (R_∞) of 0.80 and a reflectance over black (R_0) of 0.70, the printing opacity (R_0/R_∞) is 87.5, and the SX value of the paper obtained from Figure XVI-32 is found to be 2.8. Upon the addition of dyestuff, the reflectivity (R_∞) is found to be 0.75, and assuming that the SX value is not affected, R_0 is now found to be 67.9. The new printing opacity (R_0/R_∞) of the dyed paper is now found by calculation to be 90.5, compared with 87.5 before the addition of the dyestuff.

Van den Akker[263] has shown how it is possible to calculate the effect of extractives or colored additives on the color of paper by measuring the absorption coefficient (a) of the coloring matter in solution at various wavelengths. The absorption coefficient (a) is obtained by Beer's law, as follows:

$$T = C^{-acx}$$

where T is the transmittance of the solution, x is the thickness of solution, c is the concentration, and a is the absorption coefficient. K has been shown to be equal to $2a$, so that measuring the variation of $2a$ with wavelength gives a means of measuring the contribution of the coloring matter to the color of the paper. Calculations are simplified if weight is expressed in grams per square centimeter.

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[262] P. Nolan, *Paper Trade J. 105*, No. 14: 204–207 (Sept. 30, 1937)
[263] J. A. Van den Akker, *Tappi 32*, No. 11: 498–501 (Nov., 1949)

Changes in Contrast Ratio with Changes in Reflectivity. Changes in contrast ratio with changes in reflectivity of the paper can be read directly from the curves in Figure XVI-32, so long as the weight remains constant. For example, a paper having a contrast ratio of 0.80 and a reflectivity of 0.80 would have a contrast ratio of 0.84 at a reflectivity of 0.70, assuming that SX remains constant. Calculations of this type are valid only if S remains constant. The reflectivity may be changed by the addition or subtraction of dyestuff, as shown in the previous section.

Changes in Contrast Ratio with Changes in Basis Weight. For a given reflectivity (R_∞), opacity depends upon the product of S times X. Therefore, it is possible, by the use of SX, to determine from a sheet of known weight what the opacity will be at some different weight. The SX value of the paper sample at the original weight can be calculated from R_∞ and R_0 readings. The new SX value at the proposed weight can be calculated by direct proportion, since SX is directly proportional to weight. For example, assume that the paper in question has an SX value of 0.23, contrast ratio ($C_{0.89}$) of 0.80, R_∞ of 0.80, and a basis weight of 23 lb. The problem is to find what the contrast ratio of the paper would be at a basis weight of 30 lb. when the reflectivity remains constant. The new SX value will be $(0.23 \times 30)/23 = 0.30$. Using the curves in Figure XVI-32, the contrast ratio at $R_\infty = 0.80$, and at the new SX value of 0.30, is found to be 0.86. Thus, changing the weight from 23 lb. to 30 lb. would increase the contrast ratio from 0.80 to 0.86. The soundness of this type of calculation is based on the fact that S and R_∞ do not change with increase in weight, and hence can be used as constants in the calculations.

Other Uses of Kubelka and Munk Theory. By using Figure XVI-32, it is possible to obtain considerable information about a given paper more or less directly from the charts. For example,[264–266] reflectivity (R_∞) may be read directly from values of reflectance (R_0) and $C_{0.89}$ (TAPPI opacity). This permits reflectivity (brightness) to be obtained from a single small sample. The printing opacity (R_0/R_∞) may be obtained from values of R_0 and TAPPI opacity by first finding R_∞, as above, and then dividing into R_0. This permits printing opacity to be obtained from a small sample. If R_0 and R_∞ are given, TAPPI opacity may be obtained, even if a white backing of the proper reflectance (0.89) is not at hand.

Scattering power, SX (a pure number), may be read directly from any pair of values which serves to locate a point on the graph: for example, R_0 and $C_{0.89}$, R_0 and printing opacity R_0/R_∞, or R_0 and R_∞. Scattering co-

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[264] D. B. Judd, *Paper Trade J. 106*, No. 1: 5–12 (Jan. 6, 1938)

[265] D. B. Judd, *Paper Trade J. 100*, No. 1: 4–8 (Jan. 3, 1935)

[266] D. B. Judd, *Paper Trade J. 101*, No. 5: 58–59 (Aug. 1, 1935)

efficient, S, may be found directly in a similar way if the basis weight X is known. The S value is, as mentioned before, a fundamental constant and makes it possible to read from the graph the reflectances (R_0) and opacities at all weights of the paper.

Chemical Properties

The chemical properties of paper are derived primarily from the type of wood used, method and extent of pulping and bleaching, and type and amount of non-fibrous constituents added. The chemical properties of paper are important because they influence the physical, electrical, and optical properties of paper.

In a few grades of paper the chemical properties are as important, or more important, than the physical properties. An example is anti-tarnish paper, a special grade of paper used for the wrapping of silverware and polished steel articles. This paper must be free from sulfur and sulfides and must not contain free acids, chlorine, or strong alkalies, since these cause tarnishing or etching of the metal surface. The best grades of anti-tarnish paper are made from carefully purified and bleached rag or sulfite pulps which have been washed two or more times to remove all bleach residues. Paper to be printed with metallic printing inks or covered with "gold" foil must be similarly made, since the metal in the ink or foil will tarnish if it comes into contact with paper containing reducible sulfur as low as 2 p.p.m.[267] Some anti-tarnish papers used for wrapping silverware are impregnated with salts (e.g., copper acetate, lead acetate, or zinc acetate) which react with any hydrogen sulfide in the atmosphere to prevent the gas from coming into contact with the silver.

The amount of reducible sulfur in paper can be determined by heating the paper with aluminum foil and dilute phosphoric acid in a flask in the neck of which has been placed filter paper moistened with lead acetate solution. The amount of staining of the filter paper is compared with the results obtained in other control flasks containing known amounts of sodium thiosulfate. The amount of reducible sulfur should be less than 0.0008% for non-tarnishing papers. Papers having more than this amount of reducible sulfur will not necessarily be tarnishing. However, these papers should be tested by wetting with distilled water and then heating for three hours at 150 to 170° F. between two polished silver plates.

Other grades of paper in which the chemical properties are as important, if not more important, than the physical properties are photographic papers, reproduction papers, safety papers, papers requiring a high degree of permanence, electrical papers, papers to be impregnated with resins, and food wrapping papers. These grades must be free of deleterious chemicals and must have the proper *p*H, acidity, and filler content for the purpose for which the paper is intended.

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[267] *Paper-Maker* 57–70 (May 1, 1939)

Alpha Cellulose, Viscosity, and Copper Number of Paper

Alpha cellulose, viscosity in cuprammonium or cupriethylenediamine, and copper number determinations are sometimes made on paper to determine the probable stability of the paper. The values obtained are affected primarily by the quality of the fibrous constituents of the paper, although certain of the non-fibrous constituents exert an appreciable influence. Papers having a high alpha cellulose content or a high viscosity generally contain high-quality fiber (rag or highly purified chemical pulps) and are characterized by having a high degree of stability. Papers having a high copper number are generally lacking in stability. It has been suggested[268] that laboratory filter paper carry a maximum specification for copper number of 0.5. The copper number is influenced by the presence of non-fibrous reducing agents sometimes found in paper, for example, starch, calcium sulfite, zinc sulfide, and melamine resins.

The above tests are carried out on paper in about the same manner as on pulp, with the exception of a few minor differences in the method of preparing the sample. In the case of paper, the fibers are closely packed and are often protected by sizings or coatings, which makes it necessary that the sample be ground.[269] The results of these tests must be interpreted in light of the amount of lignin, moisture, mineral matter, and sizing agents in the paper and corrections made accordingly.

Amount of Sizing Agents in Paper

Commercial papers frequently contain sizing agents such as rosin, paraffin, starch, polyvinyl alcohol, glue, and casein. Analytical tests for determining the amount of these materials in paper are important for checking the retention and for determining the efficiency of these agents. For example, comparing the actual amount of rosin size precipitate in paper with the sizing value furnishes valuable information on the efficiency of the sizing operation. There is often considerable discrepancy between the amount of size present in the paper and the sizing value.

The amount of sizing agent present in paper is also of interest because of the effect of sizing agents on the physical properties and permanence of the paper. Rosin-sized papers sometimes carry a specification stating the *maximum* permissible rosin content. Waxed papers, on the other hand, frequently carry a specification stating the *minimum* permissible paraffin content.

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[268] B. W. Scribner and W. K. Wilson, *Research Paper 1809, Bur. Standards 39,* No. 1: 21–27 (1947)

[269] J. O. Burton and R. H. Rasch, *Paper Trade J. 93,* No. 4: 41–48 (July 23, 1931)

The methods of analyzing for different sizing agents have been mentioned briefly in other sections of this book. The methods are specified in detail in TAPPI Standards.

Moisture Content

The cellulose-water relationship is the most important relationship in paper chemistry. The amount of water in the individual fibers affects the strength, flexibility, and sheet-forming characteristics of the fibers. The moisture content of paper affects the weight, strength, permanence, dimensional stability, and electrical properties of paper and is a highly important factor in the calendering, printing, coating, and impregnation of paper. Moisture content is therefore an important paper specification. In the testing of paper, it is customary to condition the paper in order to maintain a constant predetermined moisture at the time the tests are made.

The test for moisture content is generally made by drying the paper in an air-circulating oven at 100 to 105° C. for about one hour, or until constant weight is obtained. Moisture content may be reported in one of two ways, as moisture on the oven-dry weight of the paper or as moisture on the "as is" weight of the paper. The former is generally used for reporting moistures of paper on the paper machine and in computations which involve reporting the results of chemical tests on a moisture-free basis. In making moisture determinations on an oven-dry basis, a small sample (about 2 g.) is generally sufficient. The "as is" method of reporting moisture is generally used for reporting the amount of moisture in paper as delivered. In making moisture determinations by this method, a larger sample (about 50 g.) should be used. The samples should be carefully handled (preferably with rubber gloves) to avoid changes in moisture content during sampling.

Paper may hold moisture either between the fibers or within the individual fibers, the moisture in the latter case being subdivided into colloidal and capillary water. At low vapor pressures, most of the water is present as colloidal water (water absorbed at the free hydroxyls), whereas at high moisture contents, considerable capillary water (water absorbed in the pores) is present. At very high moisture contents, there is some imbibed water present.

The moisture content of paper stored under normal conditions (e.g., 50% relative humidity at 73° F.) is usually between 5 to 10%. If the paper has not been stored under standard conditions, it may have a moisture content anywhere from nearly zero up to over 20%, depending upon the humidity and temperature of the atmosphere and the type of paper. The moisture content also depends upon whether the paper has been moved from an atmosphere of higher or lower humidity, or in other words, whether equilibrium is reached by adsorption or desorption of moisture. This phenomenon is known as hysteresis. The equilibrium moisture content of standard newsprint at different relative humidities is given in Table XXXIV.[270] Papers containing less lignin than groundwood would be expected to have a somewhat lower moisture content at the corresponding relative humidities (see Table III).

TABLE XXXIV

EQUILIBRIUM MOISTURE CONTENT OF STANDARD NEWSPRINT AT DIFFERENT HUMIDITIES

Relative humidity	Moisture content on absorption, %	Moisture content on desorption, %
10	..	2.8
20	..	4.9
30	6.5	6.5
40	7.2	7.9
50	8.0	9.2
60	9.0	10.4
70	10.5	11.5
80	12.2	12.7

Kress and coworkers[271] found that for a given temperature the moisture content of paper is fairly well proportional to the relative humidity at which it is stored. Rutt[272] found that a high relative humidity is more important in getting the air to part with its moisture than the actual moisture contained in the air. On the other hand, McKee and Shotwell[273] believe that the equilibrium moisture content of paper is more nearly proportional to the absolute humidity of the air than to the relative humidity. They replotted the results of Kress for two different papers, as shown in Figure XVI-34, where it can be seen that the relationship between the logarithm of the moisture content of the paper and the absolute humidity of the air is a straight line over most of the range.

In general, most investigators[274-276] have reported that increasing temperature decreases the moisture content over most of the range when the relative humidity of the atmosphere remains constant. Below about 16° C. and above 40° C., variations in temperature affect the moisture content even at the same absolute humidity.[277] McKee and Shotwell[278] obtained contrary results in that they found under conditions of constant relative humidity that the moisture content decreases with increasing temperature only up to a temperature of 60° F., after which moisture increases with an increase in the temperature. Differences in the grades of paper used and differences in methods of testing and reporting results explain the apparently ambiguous results obtained for the effect of temperature on moisture content.

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[270] Taken from TAPPI Data Sheets

[271] O. Kress and P. Silverstein, *Paper 19,* No. 25: 13–17 (Feb. 28, 1917)

[272] A. H. Rutt, *Svensk-Papperstidn. 51,* No. 18: 413–417 (Sept. 30, 1948)

[273] R. H. McKee and J. S. G. Shotwell, *Paper Trade J. 94,* No. 22: 286–288 (June 2, 1932)

[274] A. R. Urquhart, *J. Text. Inst.* 14: T183 (1923)

[275] R. E. Wilson and T. Fuwa, *J. Ind. Eng. Chem. 14,* No. 10: 913–918 (Oct., 1922)

[276] R. H. McKee and J. S. G. Shotwell, *Paper Trade J. 94,* No. 22: 284–286 (June 2, 1932)

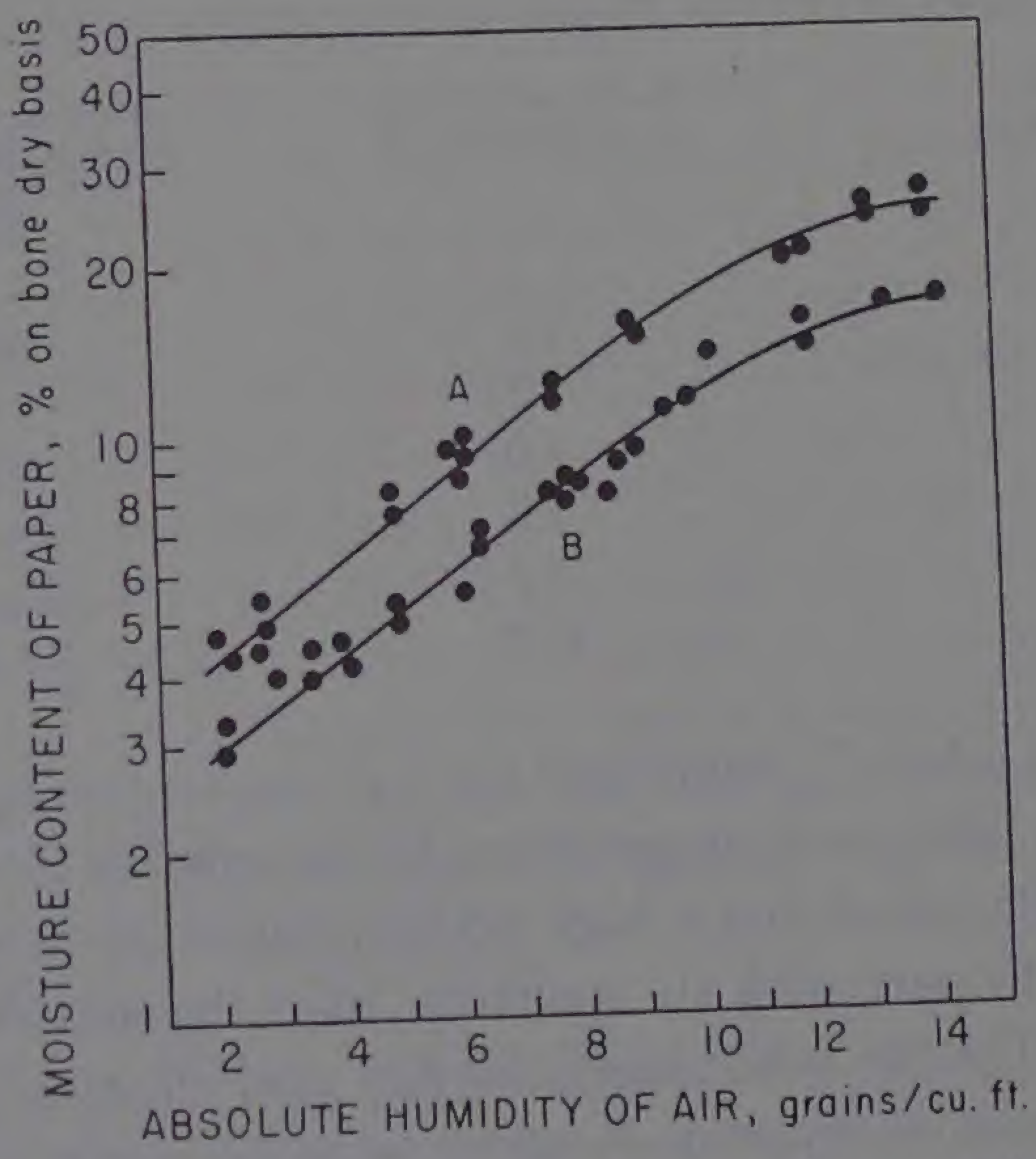

Fig. XVI-34. Effect of humidity on moisture content for newsprint (A) and book paper (B).

The rate of absorption and desorption of moisture is an important practical consideration. The rate varies slightly with different papers, depending upon the type of fibrous furnish, type and amount of sizing agents, type and amount of filler, and amount of coating.[279] Absorption of moisture is more rapid than desorption; paper tends to dry out only about one-half as fast as it picks up moisture from the same atmosphere.[280] The rate of absorption is very rapid at first, often as high as 1¾% of moisture per second, but as the paper approaches equilibrium, the rate of absorption becomes much lower. The trend is essentially the same for all papers.[281] For most papers, two to three hours is sufficient to reach equilibrium, but this depends upon the initial moisture content of the paper, the rate of air circulation, and the physical form of the paper. McKee and Shotwell[282] found, in an examination of newsprint, antique laid paper, and double-coated paper, that the rate of moisture regain was highest in the case of newsprint and lowest in the case of the coated paper. Up to twenty-four to forty-eight hours may be required for certain papers to reach equilibrium with the atmosphere. Penetration of moisture into paper in roll form is, for example, much slower than penetration into paper in sheet form. Jones[283] found that it took six months for moisture to penetrate into rolls of newsprint to a depth of 5 in. when stored under conditions of high relative humidity. Preconditioned papers for printing are sometimes wrapped in special wrappers (e.g., calender-waxed papers or asphalt-laminated papers) to prevent the paper from picking up moisture. As pointed out in Chapter VI, beating has no significant effect on the equilibrium moisture content of paper, although Baird and coworkers[284] were able to show that beaten pulps have a slightly higher equilibrium moisture content than unbeaten pulps.

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[277] R. H. McKee and J. S. G. Shotwell, *Paper Trade J. 94*, No. 22: 284–286 (June 2, 1932)

[278] *Idem.*

[279] R. H. McKee and J. S. G. Shotwell, *Paper Trade J. 94*, No. 22: 286–288 (June 2, 1932)

[280] *Idem.*

The composition of the paper affects the equilibrium moisture content, although it has less effect than the relative humidity and temperature of the atmosphere. Groundwood papers tend to absorb more moisture than unbleached chemical wood fibers, and unbleached wood fibers tend to absorb more moisture than bleached fibers (see Table III).[285, 286] Lignin appears to be the agent responsible for the high absorption of moisture by unbleached fibers.[287] Baird and coworkers[288] obtained a marked decrease in the hygroscopicity of spruce and fir sulfite pulps when the lignin was removed by bleaching, as in Table XXXV taken from part of their data.

Jarrell[289] found that the ash content of paper is a more important factor than the fiber furnish in determining the equilibrium moisture content. Fillers appear to lower the equilibrium moisture content of the paper at any

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[281] R. H. McKee and J. S. G. Shotwell, *Paper Trade J. 94*, No. 22: 286–288 (June 2, 1932)

[282] *Idem.*

[283] D. Jones, *Paper Trade J. 111*, No. 5: 57–60 (Aug. 1, 1940)

[284] C. O. Seborg, F. A. Simmonds and P. K. Baird, *Ind. Eng. Chem. 28*, No. 11: 1245–1250 (Nov., 1936)

[285] H. Fay, *Zellstoff u. Papier 6:* 201–203 (1926)

[286] C. O. Seborg, F. A. Simmonds and P. K. Baird, *Paper Trade J. 107*, No. 19: 223–228 (Nov. 10, 1938)

[287] R. E. Wilson and T. Fuwa, *Ind. Eng. Chem. 14*, No. 10: 913–918 (Oct., 1922)

[288] C. O. Seborg, F. A. Simmonds and P. K. Baird, *Ind. Eng. Chem. 28*, No. 11: 1245–1250 (Nov., 1936)

[289] T. D. Jarrell, *Paper Trade J. 85*, No. 3: 23-27 (July 21, 1927)

TABLE XXXV

EFFECT OF BLEACHING ON HYGROSCOPICITY OF SPRUCE SULFITE

Per cent relative humidity 25° C.	Unbleached		Bleached	
	Desorption	Adsorption	Desorption	Adsorption
95	32.50	22.27	30.70	20.00
87	20.90	14.60	19.03	13.47
74	14.43	10.50	13.27	9.89
56.5	9.43	7.23	....	....
53	....	....	8.13	6.50
40	6.63	5.57	5.93	5.07
12	2.77	2.40	2.30	2.07

given humidity, although the effect depends upon the type of filler used.[290] Rosin sizing does not appreciably influence the rate of moisture absorption[291] or the equilibrium moisture content.[292] Surface sizing with either starch or animal glue has little or no effect on the equilibrium moisture content of paper, although the presence of glue tends to slow up the rate of moisture absorption. The presence of hygroscopic agents in the paper, such as glycerine or corn syrup, has a pronounced effect on the moisture content. The presence of these agents increases the moisture content at high humidities and, in general, helps to stabilize the moisture content throughout a range of relative humidity of 20 to 70%.[293]

As previously pointed out, moisture affects the rigidity, flexibility, and elasticity of paper, particularly below a moisture content of about 3%. The effect of relative humidity on the physical properties of an offset paper are shown in Figure XVI-35 where it can be seen that fold and tear are the properties particularly affected by changes in relative humidity. Most of the strength properties pass through an optimum at some intermediate relative humidity. Maximum bursting strength is obtained at about 35 to 40% relative humidity on adsorption and 30% on desorption, corresponding to a moisture content of about 6%.[294] At humidities outside the range of 25 to 65%, bursting strength falls off rapidly.[295] Tensile strength passes through a maximum at a relative humidity of about 30 to 35%. At high humidities, the loss in tensile strength is greater than the loss in bursting strength. This difference is due to the stretch factor involved in the bursting strength test. The loss in tensile strength may be as much as 30% at humidities over 85%. The decrease in tensile and bursting strength at high relative humidities occurs in spite of the fact that the individual fibers in the paper increase in strength under these conditions. The loss in sheet strength must therefore be attributed to a loss in fiber friction resulting from films of water absorbed on the surface of the fibers.

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[290] H. O. Ehrisman, *Paper Trade J. 103,* No. 1: 1–4 (July 2, 1948)

[291] P. Klemm, Wochbe. *Papier-Fabr. 42:* 2105–2108 (1911)

[292] A. Arendt and E. Wathelet, *Mon. papeterie belge 12:* 105–113 (1932)

[293] J. F. Leete, *Paper Mill 58,* No. 28: 20–21 (July 13, 1935)

[294] C. O. Seborg, R. H. Doughty and P. K. Baird, *Paper Trade J. 97,* No. 15: 171–174 (Oct. 12, 1933)

[295] *Idem.*

Folding endurance improves as the relative humidity of the conditioning atmosphere is increased from zero to about 70 to 90%. The increase is particularly great between 40 and 65% relative humidity.[296] The increase in folding endurance with increasing relative humidity is due to an increase in the flexibilty of the fibers. However, at very high humidities, the tensile strength of the paper is reduced to a point where the specimen breaks after relatively few folds. The stretch of paper increases almost continuously as the relative humidity is increased from 15 to 90%. The effect of humidity on the stress-strain properties of paper has been shown in Figure XVI-7,

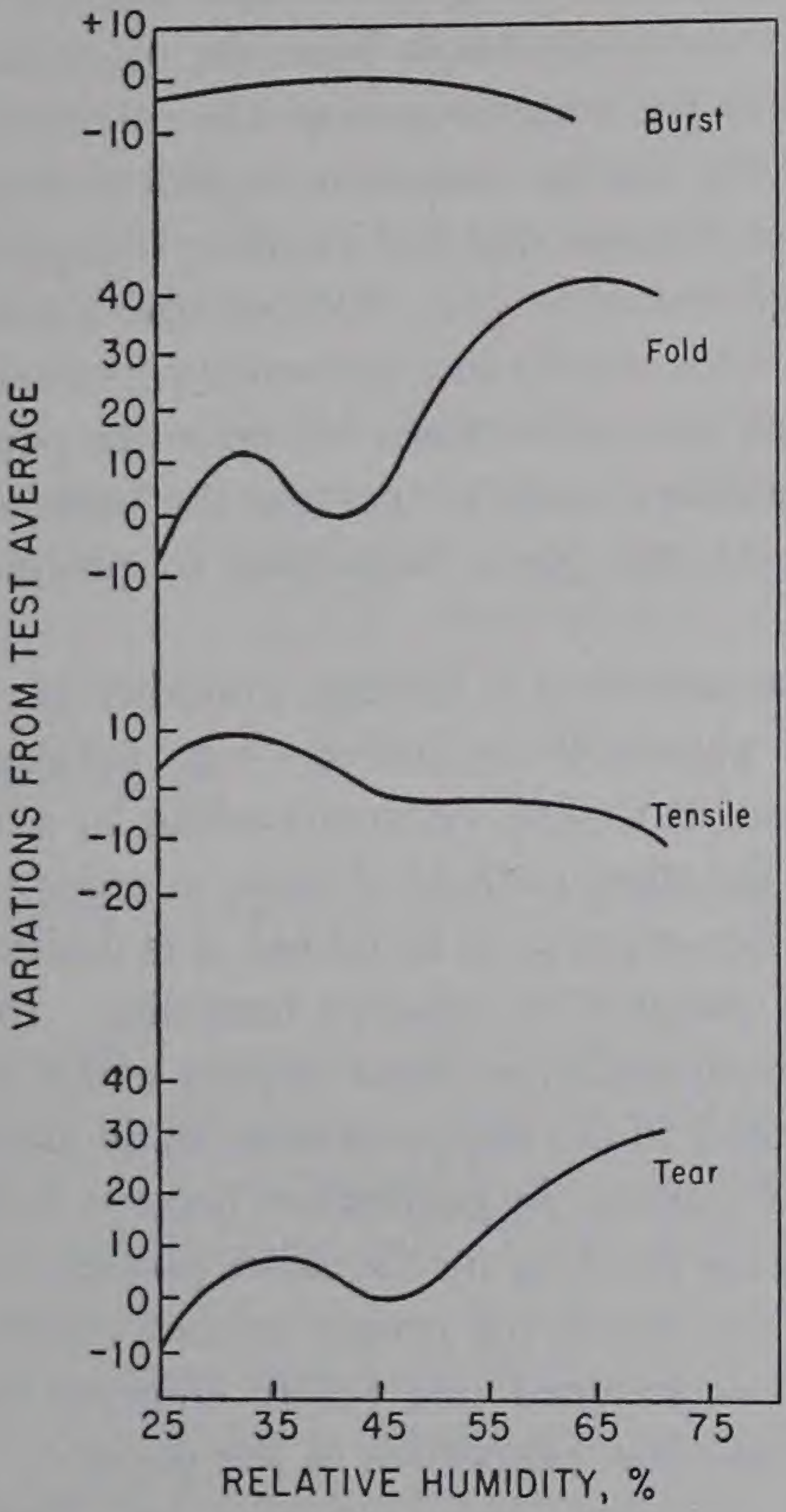

Fig. XVI-35. Effect of relative humidity on physical properties of offset paper (test average taken at 45% R. H.).

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[296] E. O. Reed, *Paper Trade J. 79,* No. 25: 227–229 (Dec. 18, 1924)

where it can be seen that the paper exhibits greater flow at the higher moisture contents. Increasing moisture content reduces the porosity and the oil permeability of the paper.[297]

It can be seen from the above that paper should have a certain minimum moisture content to be at its best. Paper should never be overdried on the paper machine, since this results in a more or less permanent loss in strength and flexibility. Cheap paperboards, such as bogus wrapping, are particularly affected by overdrying. In some cases, overdried paperboard may crease properly when first taken from the machine because of the surface moisture added at the water boxes on the calender stack, but after the board has aged and the surface moisture is absorbed into the body of the board, the fibers again become dry and brittle. If paper has been overdried, conditioning at a high humidity (i.e., 90% or over) and then bringing back to normal humidity often results in a permanent increase in strength, on account of the release of internal stresses set up in the paper during drying.[298] In addition, this procedure tends to increase the bulk and decrease the surface finish, because of the fibers returning to positions occupied before calendering.

Paper should be stored at a relative humidity of 40 to 60%.[299] The moisture content of papers to be folded (e.g., folding boxboard) should never fall below about 6 to 7% (corresponding to a relative humidity of about 50%), except for short periods of time, in order to avoid trouble with poor bending.[300] When paper is to be folded, it is desirable to do the folding in an atmosphere of about 65% relative humidity. Printing papers must have a certain minimum moisture, since papers which are too low in moisture are brittle and tend to develop excessive static electricity on the printing press.[301] Coated papers, in particular, become brittle and susceptible to cracking. Papers for printing by the offset process tend to pick up moisture and curl if they are not at the proper moisture content before printing. Corrugating papers are steamed just before entering the corrugating rolls in order to increase the flow properties of the paper.

Ash

The ash in paper may be derived from (*1*) ash in the fiber, (*2*) ash from pigments used in filling, (*3*) ash from sizing agents, (*4*) ash from mineral matter originally present in the fresh water, (*5*) ash from pigments used in coating, (*6*) ash from alum used in setting the size, and (*7*) ash derived from metallic matter from piping and machinery.

[297] G. L. Larocque, *Pulp Paper Mag. Canada 38,* No. 2: 77–84 (Feb., 1937)

[298] C. O. Seborg, R. H. Doughty and P. K. Baird, *Paper Trade J. 97,* No. 15: 171–174 (Oct. 12, 1933)

[299] T. G. Hicks, *Paper Trade J. 129,* No. 22: 474–477 (Dec. 1, 1949)

[300] W. Sooy, *Paper Mill 63,* No. 33: 12–13 (Aug. 17, 1940)

[301] W. H. Dahl, *Paper Trade J. 108,* No. 26: 329–332 (June 29, 1939)

Normally, the ash from unfilled or uncoated papers is not over 2% and is light and fluffy in appearance, although in rare cases the ash of unfilled paper may be as much as 5%. If the ash content is over 5% and is dense and compact in appearance, it may be taken as positive evidence that the paper is filled or coated. Printing papers for letterpress generally have an ash content of 15 to 25% because of the pigments used in filling. Book papers for offset generally have an ash of 8 to 15%. Pigment-coated papers generally have an ash content of 20 to 45% or more, due to the pigment used in the coating and also to the pigment used in filling. Pigment (clay) content of several typical coated papers is given in Table XXXVI.[302] Bond and writing papers have an ash content which generally ranges from 2 to 6%, although opacified bond paper may carry a specification of 6% minimum ash content.

TABLE XXXVI

CLAY CONTENT OF SEVERAL TYPICAL COATED PAPERS

Paper grade	Basis weight of base paper, lb.	Weight of filler clay, lb.	Weight of coating clay, lb.	Total clay in paper, %
Litho-coated one side	43	2.15	14.45	27.7
Letterpress-coated two sides ...	45	4.05	22.50[a]	37.1[a]
Machine-coated magazine-coated two sides	39	4.30	13.6	32.6

[a] In this case, the weight is not all due to clay; the coating contains 5.62 lb. of another pigment.

Papers made for high strength (e.g., wrapping papers and container boards) should have a low ash content, since mineral matter tends to reduce the strength of paper. High ash content is also undesirable in photographic papers and electrical insulation papers. Filter papers used for analytical work must contain a negligible amount of ash, and consequently these papers are extracted with hydrochloric and hydrofluoric acids.

The amount of ash in paper is determined by igniting a known weight of the paper in a platinum, alundum, or silica crucible, using a Meker burner or an electric muffle at about 925° C. Ignition is carried out until the ash is free from specks of carbon, which generally requires about thirty to sixty minutes. Ordinarily, the ash will be white in color, but if colored pigments are present in the paper, the ash will be colored. The results are reported as the percentage of ash to the nearest 0.1% on the basis of the oven-dry paper, obtained by correcting for the moisture in the paper. When special accuracy is desired, the paper may be weighed out in the oven-dry condition and the results reported to the nearest 0.05%.

An ash determination tells nothing about the nature of the ash. It is important, however, to identify the source of the ash, since ash from residual chemicals left over from bleaching or dyeing is more harmful to the strength and permanence of paper than clay or other fillers. Identification of the ash is also desirable when trying to match competitive papers. Regular qualitative procedures can be used for identifying the constituents in paper ash. A suitable procedure is outlined in TAPPI Standards for identifying the common pigments used in papermaking. Special tests are also described for measuring the amount of arsenic, titanium, acid-soluble iron, and similar materials. In carrying out qualitative tests, portions of approximately the same size should be used throughout the procedure so that reliable estimates can be made of the relative quantity of the different substances which are present. The report should include a list of all the cations and anions found in the ash, as well as an approximate indication of the amounts of each. In addition, the report should list the pigments present in the paper as indicated by the most likely combination of the ions.

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[302] "Kaolin Clays and Their Industrial Uses," p. 127, J. M. Huber Corp., New York, N. Y. (1949)

The presence of considerable amounts of aluminum and silica indicates the presence of clay. Titanium indicates the presence of titanium dioxide, or one of the titanium composite pigments; for example, titanium and barium indicate the presence of titanium dioxide-barium sulfate, whereas titanium and calcium indicate the presence of titanium dioxide-calcium sulfate. Papers containing titanium dioxide appear dark under ultraviolet light since titanium dioxide absorbs ultraviolet rays. An alkaline ash containing calcium soluble in hydrochloric acid, but no sulfate, indicates the presence of calcium carbonate. (If carbonate is present, the paper should liberate carbon dioxide when acidified.) The presence of calcium and sulfate in the ash soluble in hydrochloric acid indicates the presence of calcium sulfate (gypsum or crown filler). The presence of calcium and sulfur dioxide indicates the presence of calcium sulfite. (Papers containing calcium sulfite liberate sulfur dioxide when acidified.) The presence of sulfide and zinc indicates the presence of zinc sulfide or lithopone (zinc sulfide and barium sulfate). The presence of barium and sulfate in the acid-insoluble portion of the ash indicates the presence of barium sulfate (blanc fixe or barytes). The presence of barium in the ash soluble in hydrochloric acid (with effervescence) indicates the presence of barium carbonate or witherite. The presence of aluminum, calcium sulfate, and carbon dioxide in coated paper indicates the presence of satin white. The presence of silica alone indicates the presence of diatomaceous earth. The presence of considerable amounts of magnesium and silica indicates the presence of magnesium silicate (talc, agalite, or asbestine).

Traces of various minerals should be reported, even though these are generally due to impurities in the pigments, fibers, or in the water. Nearly all papers contain traces of calcium, magnesium, and sulfate ions picked up from the mill water. Some of the impurities commonly associated with the various commercial pigments are as follows:

Pigment	Impurities present
Clay	Ca Mg Ti
Titanium dioxide	Al SO_4
Satin white	CO_3
Calcium sulfate	Mg
Calcium sulfite	SO_4

Aluminum is almost always present in paper ash because of the alum used in setting rosin size.

In addition to the regular qualitative tests, semi-micro techniques have been developed in which the centrifuge is used in place of filtering for concentrating precipitates. Simple qualitative tests for the most important fillers in paper, based upon examination of the ash under the microscope, are given below. This method is very rapid, because identification is based upon the crystal structure of the pigments. The reactions are carried out in small drops on microscope slides. By using such amounts of materials, evaporations and fusions can be carried out in a fraction of the time required for a regular chemical analysis. Another advantage of microscopic analysis is that it permits distinguishing between the natural and artificial pigments which have the same chemical composition, but different physical form. The refractive index of any pigment can be determined by mounting some of the pigment in liquids of known refractive index. For double refractive materials, polarized light can be used.

Clay, talc, and asbestine can be readily recognized by the appearance of the particles when mounted in water and examined under high power. The flat plates of kaolin and mica are characteristic of china clay. The particles of talc are larger and more or less fibrous, asbestine being very fibrous.

If calcium is suspected, some of the ash should be added to a drop of water on the slide. A few crystals of iodic acid are then added and the slide scratched to start crystallization. If calcium is present, calcium iodate forms as colorless diamond-shaped crystals with high double refraction. If calcium carbonate is present, the iodic acid will cause effervescence. Often, however, the carbonate is destroyed when the paper is ashed. In this case, the ash will give a strongly alkaline reaction with phenolphthalein.

If titanium is suspected, some of the ash should be added to a drop of dilute sulfuric acid on one corner of the slide. Some ammonium sulfate should then be added and the mixture evaporated and heated carefully until strong fumes appear. The mixture is then cooled and distilled water is added to make a drop about the same size as the original drop. A drop of hydrogen peroxide is added. Yellow color shows the presence of titanium.

If zinc is suspected, some of the ash should be added to a drop of dilute nitric acid on one corner of the slide. This should be evaporated to dryness and a second drop of dilute nitric acid added and again evaporated to dryness. This is then repeated for a third time. Finally, a drop of water and a trace of acetic acid are added. In another drop of water on the same slide, some potassium mercuric sulfocyanate is dissolved and this drop is then flowed into the other. Zinc mercuric sulfocyanate separates as characteristic feathery crystals which are white by reflected light, and black by transmitted light.

If barium is suspected, some of the ash should be added to a drop of dilute sulfuric acid on the corner of slide. This should then be evaporated until strong fumes appear. When partly cool, breathing on the slide will start crystallization. Barium sulfate crystallizes as feathery crosses with a marked tendency for two adjacent arms to be longer than the others. Calcium sulfate crystallizes as rounded grains with hair-like projections on each end.

For further information on the methods of examination and for pictures of the various types of crystals, the reader is referred to other sources.[303, 304]

For mineral matter which is not decomposed by heat (e.g., titanium dioxide), the weight of the ash may be taken as the weight of the pigment present. Clay is not changed chemically on ignition, but there is a loss in water of hydration. It has been reported that ashing at 800° C. causes clay to lose 12.5% water, talc 1.5%, and magnesium carbonate almost 50%.[305] Many pigments are changed chemically by ashing, and hence the weight of ash cannot be reported as the weight of pigment; for example, calcium sulfate is decomposed at 1200° C. to calcium oxide, barium sulfate is decomposed at 1510° C. to barium oxide, calcium carbonate is decomposed at 825° C. to calcium oxide, and zinc sulfide sublimes at 1185° C. Suitable correction factors must be applied when ashing papers containing the above pigments if it is desirable to convert the values obtained to amount of the corresponding pigment. These factors can be obtained from ignition tests made on known quantities of the pigment. For pigments such as calcium sulfate and barium sulfate, the ignition test should be made in the presence of paper in order to simulate the reducing atmosphere.

Often it is necessary to determine the relative proportion of two or more pigments in paper. This can be done by appropriate quantitative procedure, but this is complicated, and generally simpler methods are used.

[303] E. M. Chamot and C. W. Mason, *Handbook of Chemical Microscopy*, Vol. II, John Wiley & Sons, New York (1931)

[304] K. P. Geohegan, *Paper Trade J. 90*, No. 10: 164–166 (March 6, 1930)

[305] M. Chêne, C. Deissenberg, Canaud, Martin-Borret, and Chiaverina, *La Papeterie 68:* 226–231, 258–261, 290–291, 326–329 (1946)

A common problem is to determine the ratio of clay and calcium carbonate in filled or coated papers. This can be done by determining the total ash by a regular ash determination on the paper. A second sample of the paper is then extracted with dilute hydrochloric acid to remove calcium carbonate, and then ashed. The difference between the two values gives the ash due to calcium carbonate. This value can be converted to weight of actual calcium carbonate by multiplying the weight of ash by the factor 100/56 to convert from calcium oxide to calcium carbonate. The weight of actual clay in the paper can be determined by multiplying the weight of ash obtained on the acid-extracted paper by about *1.16* to correct for the loss of water of hydration on ignition.

It is frequently desirable, in the case of pigment-coated papers, to determine whether the ash is derived from the filler or from the surface coating. This can be done by stripping the coating from the paper by soaking the paper in an enzyme solution for one hour at 50° C. and then brushing off the coating with a camel's-hair brush (see Ch. XVIII). The ash in the coating can be determined indirectly by substracting the ash of the decoated paper from the total ash of the original paper.

Acidity and pH

The acidity is important because of its effect on the permanence of paper. The acidity may be determined as water-soluble acidity (or alkalinity), or as the hydrogen ion concentration (*p*H) of the paper extract. The hydrogen ion concentration (*p*H) is more indicative of the stability of paper than the total acidity.

Water-soluble acidity is determined by grinding the paper and digesting in boiled distilled water for one hour under reflux at 98 to 100° C. The digested fibers are then filtered on a Buchner funnel (without filter paper), and the resulting extract is titrated with either 0.01 *N* NaOH or 0.01 *N* HCl, as the case warrants, using phenolphthalein as the indicator. The results are reported as per cent of SO_3 or per cent of Na_2O on the basis of the moisture-free paper.

The *p*H can be determined by either hot or cold extraction. In the cold extraction, 1 g. of paper (either cut or ground) is macerated with a stirring rod in 20 ml. of distilled water at 20 to 30° C. Then, 50 ml. more of water is added and the sample is left for one hour, after which the *p*H is determined in a *p*H meter. In the hot extraction, the same procedure is followed, except that the sample is digested at 95 to 100° C. under reflux for one hour, instead of merely standing at room temperature. The hot extraction method is more widely used than the cold extraction, although the cold extraction probably gives the more nearly normal *p*H of the paper. Hot extraction ordinarily gives a *p*H about 0.5 lower than cold extraction due, according to Launer,[306] to the increased hydrolysis of aluminum salts at high temperature. In the case of wet-strength papers made with melamine-formaldehyde resin, hot extraction may give a higher *p*H than cold extraction due to hydrolysis of the resin and liberation of free melamine.[307] Because of the difference in results obtained with the two methods, the analytical report should always state which method was used. An indication of the surface *p*H of paper can be obtained by streaking the paper with indicator solution, *e.g.*, brom cresol green.

Acidity in paper is derived principally from the alum used in sizing. Acidity may also be derived from bleach residues left in the pulp, absorption of acid gases from the atmosphere, or from the presence of organic acids found in the pulp, sizing agents, or coating materials. Paper may also pick up acid by contact with the skin during handling. Filled or coated papers are likely to have a high alkalinity, due to the presence of alkaline pigments.

The *p*H is very important for bonds, ledgers, and index papers which are intended for permanent records. Some of the generally accepted specifications are as follows:

Type of paper	Minimum *p*H
Papers for permanent records	5.0
White bonds	5.0
Colored bonds	4.7

The *p*H is important in converting papers (e.g., papers for saturating, impregnating, or coating), since the *p*H is likely to affect the materials used in these converting operations. The *p*H apparently has some effect on the initial strength of the paper. Libby and Dohne[308] report that the bursting strength is reduced approximately 10% in going from a *p*H of 4 to 6 when alum is used for setting rosin size. On the other hand, the bursting strength is increased approximately 15% over the same *p*H range when alum-aluminate mixtures are used for setting the size.

Permanence of Paper

A lack of permanence in paper can be manifested either by (*1*) discoloration of the paper, (*2*) a loss in strength of the paper, or (*3*) a change in chemical properties, e.g., increase in copper number, decrease in alpha cellulose, or decrease in cuprammonium viscosity. The extent of the changes in paper on aging depends upon the type of fiber, the amount and type of secondary ingredients present, and the atmospheric conditions to which the paper is subjected. Changes are highly undesirable in papers requiring a high degree of permanence, e.g., record papers and base paper for plastics.

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[306] H. F. Launer, *Paper Trade J. 110,* No. 10: 135–140 (March 7, 1940)

[307] C. S. Maxwell and W. F. Reynolds, *Tappi 33,* No. 4: 178–182 (Apr. 1950)

[308] W. P. Dohne and C. E. Libby, *Paper Trade J. 113,* No. 22: 280–286 (Nov. 27, 1941)

The best method of measuring the permanence of paper is by natural aging. However, this method is obviously impractical for relatively permanent papers because of the time involved. In order to shorten the time involved, accelerated test methods have been devised which utilize light and heat. The instruments used for measuring the extent of color fading by light (usually from a carbon arc) are called Fade-Ometers. These lamps vary considerably in the rate at which they fade paper, due mostly to variations in line voltage, and some lamps may require from 2 to 3 times as long to produce the same fading as others.[309] One means of overcoming this difficulty is to compare the results with a paper of known fading quality. Fade-Ometers do not have the same relative spectral energy distribution as sunlight.

Heat tests may be used to measure the relative stability of paper, although heating does not always give results comparable to natural aging because of the dehydration which occurs at high temperatures. In carrying out accelerated aging tests using heat, paper strips are heated in an oven at 105° C. for seventy-two hours and then tested for folding endurance. The results are reported as per cent retention of folding endurance after the heated samples have been reconditioned under standard conditions. This test is most widely used for testing the quality of high-grade rag papers which normally retain about 90 to 100% of their original folding endurance under these conditions. The test is not suited for the testing of groundwood papers.

Klemm[310] reported as early as 1929 that pure cellulose lasts indefinitely without discoloration. Commercial papers, however, vary greatly in their resistance to aging. The grades of paper having the greatest permanence are those made from pulps possessing high cuprammonium viscosity, high alpha cellulose content, low copper number, low lignin content, and low pentosan and gamma cellulose content. The U. S. Government Printing Office carries a specification of not less than 95% alpha cellulose for rag papers (e.g., book, bond, ledger, and index papers) required for permanent records.[311] The copper number must not exceed 1.0. Groundwood papers have the lowest stability. Papers made from chemical wood pulps are much more stable than groundwood; sulfite pulps are more stable than sulfate; and lightly bleached sulfites are more stable than highly bleached sulfites.[312] Rag papers have the highest degree of permanence of the common papers, and are specified when maximum permanence is required. Mixed rag and chemical wood fibers are specified for many grades of permanent papers, and for these grades it is customary to make routine microscopic examination of the paper to see that it meets the specified fiber content.

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[309] *Paper-Maker 64,* No. 6: 52 (Dec., 1947)

[310] P. Klemm, *Paper Trade J. 89,* No. 6: 53–58 (1929)

[311] M. S. Kantrowitz, *Paper Trade J. 128,* No. 25: 231–234 (June 23, 1949)

[312] H. W. Giertz, *Svensk Papperstidn. 48,* No. 13: 317–323 (July 15, 1945) through L. E. Wise, *Paper Ind. 29,* No. 6: 825–829 (Sept., 1947)

Lignin is particularly sensitive to light and undergoes a photochemical reaction in sunlight leading to a darkening of the lignin. It is this photochemical reactivity of lignin which is responsible for the rapid deterioration of groundwood papers. The rate of fading of groundwood papers in sunlight is very rapid in the early period of exposure; it appears to be nearly proportional to the square root of the exposure time.[313] Even a small amount of groundwood in a mixed furnish has a pronounced deleterious effect on the photochemical stability of the paper. This effect on the color change is disproportionately large for small groundwood content.

The effect of light on aging depends upon wavelength. Cellulosic fabrics have, for centuries, been whitened by exposure to air and sunlight, and yet it is known that papers tend to yellow in sunlight. This apparent anomaly can be explained by the difference in effect obtained with radiations of different wavelengths. Groundwood papers have a characteristic heavy absorption of radiation in the ultraviolet region, and it is this range of wavelength which is primarily responsible for the color change on exposure to light. It has been shown[313, 314] that electromagnetic radiations of wavelength longer than 480 millimicrons have a slight bleaching effect on groundwood, in contrast to the dulling and yellowing effect which occurs at shorter wavelengths. The amount of oxygen present is a factor, since it has been shown[315] that groundwood papers fade at a slightly greater rate in the presence of oxygen.

Heat by itself, at least in certain temperature ranges, has relatively little effect on discoloration. This is demonstrated by the fact that there is no appreciable difference in brightness when papers are aged at 20° C. and at elevated temperatures, so long as aging is carried out in the dark. However, increasing the temperature in the presence of light has an accelerating effect on fading because of the effect of temperature on the photochemical reactions. The discoloration of thick insulation boards, which are commonly dried in ovens at 300 to 400° F., is a serious problem in the insulating board industry. Much of this board is made from groundwood pulp, and the discoloration comes from the lignin in the pulp. On the other hand,

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[313] J. A. Van den Akker, H. F. Lewis, G. W. Jones and M. A. Buchanan, *Tappi 32,* No. 4: 187–192 (Apr., 1949)

[314] P. Nolan, J. A. Van den Akker and W. A. Wink, *Paper Trade J. 121,* No. 11: 101–105 (Sept. 13, 1945)

[315] *Idem.*

McIntyre[316] found, in the case of sulfite pulps, that certain reactions occur in the drying of the paper (in the presence of heat and moisture) which reduce the reflectance somewhat, but tend to improve the light stability of the paper. He found that machine-dried papers have a greater stability than air-dried pulp.

In addition to the degrading effect on lignin, light also tends to degrade the cellulose, hemicelluloses, and other carbohydrates in the fiber, as well as fats, resins, and waxes. Lewis and Fronmuller[317] found that ultraviolet light from a Fade-Ometer tends to bring about a shortening of the cellulose chain molecules, although sunlight has relatively little effect on the cellulose fraction in groundwood papers. It is the light rays shorter than about 300 millimicrons which have the most detrimental effect on cellulose.[318] The offending substances in bleached wood pulps appear to be hemicelluloses,[319] and there appears to be a direct relationship between hemicellulose content and the yellowing tendency of bleached pulps. Of all the hemicellulosic materials, the degraded celluloses have the greatest effect.[320] Giertz[321] showed that yellowing in bleached pulps was caused principally by the decomposed carbohydrates produced by the bleaching operation. On the other hand, Schwalbe[322] pointed out that the addition of glucose improves the color stability of groundwood, and proposed that the mechanical pulp is more heat- and light-sensitive than the original wood because of the removal of soluble carbohydrates during grinding.

Even if the pulps used in making paper are of high purity, the paper will not be permanent if other conditions are not favorable.[323] High humidities are more detrimental to permanence than low humidities. Tongren[324] found in tests conducted at 100° C. (and relative humidities of 25% and above) that the rate of discoloration upon aging increases linearly with relative humidity. McIntyre[325] obtained a minimum aging rate with bleached sulfite pulp at a relative humidity of about 20%, as shown in Figure XVI-36. Different pulps react differently to the effect of humidity, and hence it is desirable in accelerated aging tests to maintain a normal moisture content by controlling the relative humidity to about 55%.[326] The presence of excessive moisture at elevated temperatures promotes a hydrolytic attack on the fibers. Papers for permanent records should be kept at constant relative humidity, since frequent changes in humidity result in repeated expansions and contractions of the paper, causing excessive wear on the fibers. For this reason, valuable historical documents are generally kept in rooms maintained at constant relative humidity.

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[316] J. W. McIntyre, *Paper Trade J. 109*, No. 24: 317–325 (Dec. 14, 1939)

[317] H. F. Lewis and D. Fronmuller, *Paper Trade J. 121*, No. 14: 133–136 (Oct. 4, 1945)

[318] W. Hirschkind, D. J. Pye and E. G. Thompson, *Paper Trade J. 105*, No. 18: 268–269 (Oct. 28, 1937)

[319] H. W. Giertz, *Svensk Papperstidn. 48*, No. 13: 317–323 (July 15, 1945)

[320] H. H. Houtz and E. F. Kurth, *Paper Trade J. 109*, No. 24: 326–329 (Dec. 14, 1939)

[321] H. W. Giertz, *Svensk Papperstidn. 48*, No. 13: 317–323 (July 15, 1945) through L. E. Wise, *Paper Ind. 29*, No. 6: 825–829 (Sept., 1947)

[322] C. G. Schwalbe, *Papier-Fabr. 35*, No. 27: 243–247 (Fest-u. Auslandheft, 1937)

[323] C. A. Blaisdel and J. E. Minor, *Paper Ind. 15*, No. 9: 512–514 (Dec., 1933)

[324] J. C. Tongren, *Paper Trade J. 107*, No. 8: 76–84 (Aug. 25, 1938)

[325] J. W. McIntyre, *Paper Trade J. 109*, No. 24: 317–325 (Dec. 14, 1939)

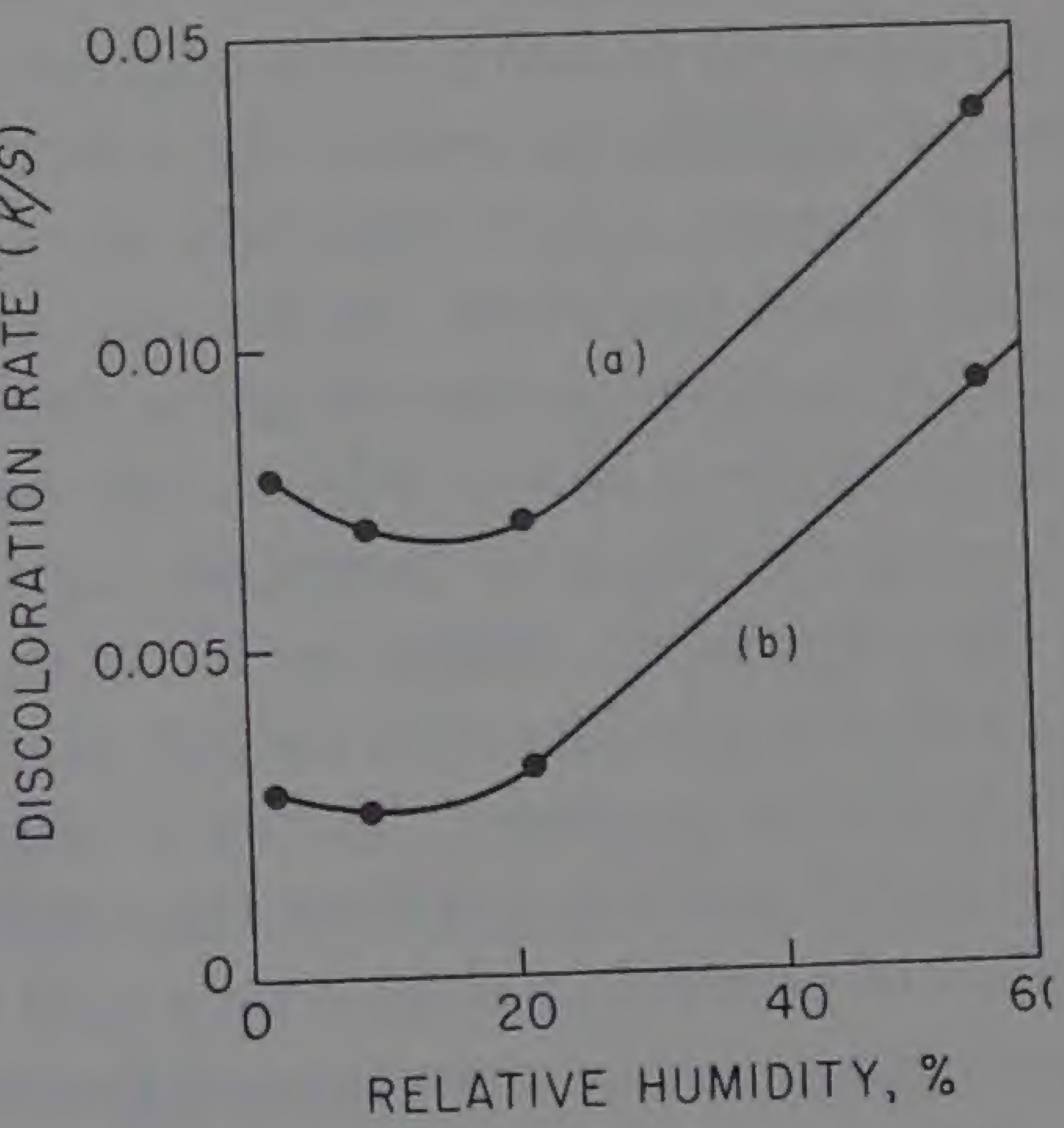

Fig. XVI-36. Effect of relative humidity on the discoloration rates of air-dried (a) and machine-dried (b) pulps.

The effect of *p*H on the stability of paper is well known, and today, chemical wood and rag papers for permanent records are made with a *p*H value within the range of 5.0 to 7.0 On the other hand, groundwood papers appear to have their greatest brightness at a *p*H around 4.0.[327] One effect of long exposure of paper to sunlight is a lowering of the *p*H of the paper. Even sulfur dioxide in the atmosphere will cause deterioration of paper;[328] and sulfur dioxide and iron in the same paper are particularly harmful.[329] Iron produces considerable discoloration on aging. Bleach residues left in the pulp from the bleaching operation cause discoloration and loss in strength.

Rosin size lowers the permanence of paper; a high percentage of rosin results in a yellowing of the paper on aging, as well as a loss in strength (particularly folding strength). Tongren[330] obtained a straight-line relationship between the rosin content of paper and the aging rate (change in K/S number) when the two were plotted on log paper. The degradative effects of rosin are due to oxidation, and consequently, papers sized with modified rosins are considerably more stable than papers sized with natural rosin. Starch and animal glue have no degradative effect in themselves, but in cases where the fold and bursting strengths are due in part to surface sizing with these materials, there is a tendency for the strength to decrease on aging. Writing inks, especially those of low pH, increase the rate of deterioration of paper on aging. On the other hand, coatings, lacquers, or printing on the surface of the paper often act as protective layers and reduce the amount of deterioration on aging.

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[326] J. W. McIntyre, *Paper Trade J. 109*, No. 24: 317–325 (Dec. 14, 1939)

[327] J. A. Van den Akker, H. F. Lewis, G. W. Jones and M. A. Buchanan, *Tappi 32*, No. 4: 187–192 (Apr, 1949)

[328] A. E. Kimberly and A. L. Emley, *Bur. Standards, Misc. Publ. No. 140,* 7 pp. (1933)

[329] L. K. Johnson, *Paper Trade J. 108*, No. 26: 333–337 (June 29, 1939)

[330] J. C. Tongren, *Paper Trade J. 107*, No. 8: 76–84 (Aug. 25, 1938)

Fillers have little degradative effect on paper. In fact, the alkaline fillers tend to prolong the life of the paper.[331] Zinc sulfide is supposed to increase the permanence of paper by absorbing some of the harmful light rays. The effect of dyestuffs on permanence of cellulose is not well understood. It is possible that certain dyestuffs protect cellulose from the destructive effects of light. Other dyestuffs are apparently capable of transforming absorbed radiant energy in such a way as to cause deterioration of the fiber. It has been reported[332] that direct dyes protect cellulose, whereas acid dyes are harmful.

Odor and Taste

Odors and tastes are very difficult to describe, either for quality or intensity. There are no basic units in which these properties may be expressed, and hence there is no method by which they may be classified or compared, except in the personal opinion of the tester. An expert who can classify odors and thus help to track down their origin is invaluable at times.

Paper and paperboard readily absorb tastes and odors. As a rule, paper does not hold tastes or odors permanently, but rather tends to transfer them to other absorbent materials. Hence, foodstuffs packaged in paper or paperboard containers tend to pick up tastes and odors from the package. For this reason, paperboard used for packaging foodstuffs should be lined with high-grade virgin pulp or the inner surface protected in some way. Often, paperboard for packaging is coated with a thin film of sodium silicate or starch on the side which comes in contact with the food product.

Several odor transfer tests are used for the detection of off-odors in paper. Butter or plain milk chocolate placed in contact with (or stored in a closed container with) the suspect paperboard is a rather sensitive test, since these substances are easily upset in flavor balance by a small amount of off-odor substance. Attempts have been made to isolate and classify the odor constituents of paper by absorbing or dissolving these constituents in different solvents or media, but the results are rather inconclusive.

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[331] T. D. Jarrell, F. P. Veitch, *U. S. Dept. Agr., Tech. Bull. 541T,* 20 pp. (1936)
[332] *Textile Weekly 30:* 164–167 (1942)

Every effort should be made to eliminate the source of odor or taste in paper. Paperboard itself generally has an odor described as "paper odor," but this is ordinarily not objectionable, since this type of odor is low in intensity and not readily picked up by foodstuffs. This odor varies according to the type of pulp used; for example, paper made from alpha pulp is practically odorless, whereas paper made from kraft pulp has a typical sweet coumarin mercaptan-like odor.[333] One source of taste and odor in paper is the process water, and for this reason, the process water should be carefully treated, particularly if the paper is to be used for the packaging of food products. In addition to odor picked up from water, disagreeable musty, sour, or putrid odors may be imparted to paper as a result of slime growth in the mill system, decomposition of oils in groundwood pulps, spoiled starch or protein sizing agents, and other similar sources. Papers surface-sized with glue or papers coated with casein frequently have an objectionable musty odor, particularly during the summer months.[334] Toxicants added to control slime growth may impart a chemical or "medicinal" odor to the paper. The printing on the paper may be responsible for odor. Other sources of odor are anti-foaming agents, dispersing agents, foreign matter added with waste paper stock, and contaminants such as oil and kerosene.

Electrical Properties

Paper is among the cheapest and best electrical insulating materials known. Although the amount of paper consumed in the electrical field is not large compared with other fields, paper is a very important insulating material in the radio, telephonic, and similar fields.

Electrical papers must meet certain physical and chemical standards and, in addition, must meet specifications on electrical properties. Electrical properties are, in general, dependent upon the physical and chemical properties of the paper. For many purposes impregnated papers are used. The important electrical properties for a good electrical insulation paper are: (*1*) high dielectric constant (specific inductive capacity), (*2*) high dielectric strength (electrical resistance), (*3*) low power factor (dielectric loss), and (*4*) freedom from conducting particles. The electrical properties of cellulose and a typical insulating paper are given in Table XXXVII.[335]

The ultimate value of electrical papers is determined by the life of the paper under the particular conditions of use. The physical life of electrical

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[333] Report on talk given by L. B. Sjöström, *Tappi 33,* No. 6: 58A, 60A (June, 1950)

[334] L. K. Johnson, *Paper Trade J. 108,* No. 26: 333–337 (June 29, 1939)

[335] G. T. Kohman, *Ind. Eng. Chem. 31,* No. 7: 807–817 (July, 1939)

TABLE XXXVII

DIELECTRIC PROPERTIES OF CELLULOSE AND PAPER

Sample	Dielectric constant	Power factor	Resistivity, ohms/cm.	Dielectric strength, volts, d.c.	Density
100% cellulose	8.1	....	10^{18}	25×10^6	1.56
Paper	1.2–4	0.001–0.002	$> 10^{18}$	2×10^5	0.2–1.2

equipment depends upon the life of the paper used as the insulation. In a.-c. units, life is affected principally by the magnitude of the dielectric loss, whereas in d.-c. units, life is a function of degradation and points of low resistivity.[336] The temperature of insulation in use is generally about 100° C.,[337] and consequently electrical insulation paper should be as free as possible of chemical deterioration resulting from high temperature. Impregnated papers generally have a shorter life than unimpregnated papers.

Specific Inductive Capacity (Dielectric Constant)

Specific inductive capacity is related to capacitance. Capacitance is defined as the ratio of the charge on a condenser to the potential difference between the terminals of the condenser. The specific inductive capacity (dielectric constant) of paper is the ratio of the capacitance of a two-plate electrical condenser when the space is filled with the paper to the capacitance when the space is under vacuum.

Pure cellulose has an exceptionally high dielectric constant which is due, in all probability, to the oscillation of polar hydroxyl groups on the cellulose molecules, or to strongly adsorbed moisture.[338–340] The most reliable value for the dielectric constant for solid native cellulose appears to be 6.0 to 6.1.[341] The dielectric constant of paper is much lower, generally varying from slightly over 1 to about 2.5[342] The specific inductive capacitances of a few common materials are given in Table XXXVIII. The dielectric constant of cellulose increases with increasing temperature.

Paper has a lower dielectric constant than pure cellulose because of the high percentage of air voids in the paper. To overcome the low dielectric strength, paper used for insulation in power transmission cables, or as the dielectric in wound capacitors, is impregnated with oil, wax, or certain

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[336] C. Delevanti, Jr., and P. B. Hansen, *Paper Trade J. 121,* No. 26: 241–249 (Dec. 27, 1945)

[337] C. H. Pike, *Paper-Maker 111,* No. 1: 11–12 (Jan., 1946)

[338] G. T. Kohman, *Ind. Eng. Chem. 31,* No. 7: 808–817 (July, 1939)

[339] A. Campbell, *Proc. Roy. Soc.* (London) *A78:* 196–211 (1907)

[340] H. A. DeLuca, W. B. Campbell and O. Maass, *Can. J. Research 16,* Section B, No. 8: 273–288 (Aug., 1938)

[341] C. R. Calkin, *Tappi 33,* No. 6: 278–285 (Jan., 1950)

[342] C. Delevanti, Jr., and P. B. Hansen, *Paper Trade J. 121,* No. 26: 241–249 (Dec. 27, 1945)

TABLE XXXVIII

SPECIFIC INDUCTIVE CAPACITANCES OF SEVERAL COMMON MATERIALS

Dry air	1.0 (approx.)
Paraffin	2.1-2.2
Wood	2-6
Glass	5-9
Paper	1-2.5
Pure cellulose	6-7
Paper fibers	About 5.5

resins, because these materials have greater specific inductive capacity than air. Impregnation raises the dielectric constant of paper and results in a more equitable distribution of the electric field. However, any gain in capacitance by increasing the specific inductive capacity of the impregnant is limited by that of the paper, since combination paper-oil dielectrics behave as a series.[342] Residual gas (air) in impregnated papers is a cause of poor performance.

Dielectric Strength

The dielectric strength of paper is measured by the ability of the paper to offer resistance to the passage of electrical spark discharge. The dielectric strength can be determined by placing a specimen of paper of known thickness between electrodes and subjecting it to voltage stress until breakdown occurs.[343]

In practice, a high dielectric strength is required in condenser papers and insulating papers to be used under conditions of high voltage. At high voltage, charges are built up on the fiber surface, negative charges on one side of the fiber, and positive on the other. Because of the internal resistance of the fibers, these charges do not neutralize one another, but rather they act to oppose the electric field presented by the material in the voids of the paper, i.e., air or oil. At the same time, however, the field within the fiber itself is intensified, and eventually (at very high voltages) the dielectric strength of the fiber is exceeded and the fiber breaks down. Once the dielectric strength has been exceeded, a permanent change is wrought in the paper and it no longer has the same dielectric strength. This point is referred to as the breakdown strength of the paper and is dependent on the breakdown strength of the fiber itself.[344] The dielectric strength is expressed in terms of the total voltage at breakdown divided by the thickness of the paper.

The most important individual sheet factor contributing to the dielectric strength of paper is the dielectric strength of the individual fibers.[345]

[343] D. O. Adams, *Paper Trade J. 122,* No. 7: 63-72 (Feb. 14, 1946)

[344] *Idem.*

[345] J. A. Van den Akker, *Paper Trade J. 119,* No. 26: 253-255 (Dec. 28, 1944)

In the case of impregnated papers, the dielectric strength is a complex function of the dielectric strengths of both the paper and the impregnant.[346] The dielectric strength of impregnated papers decreases with an increase in sheet density,[347-349] due apparently to the increased percentage of fiber to impregnant. In general, the dielectric strength decreases with an increase in the thickness of the paper, because of the greater proportion of fiber to air as the thickness is increased. The time of voltage stress and frequency affect the dielectric strength.

Dielectric Loss (Power Factor)

Dielectric loss is an important consideration in capacitor paper, because losses represent energy loss which must be dissipated as heat, a problem in capacitors. The heat generated per unit of volume is proportional to the square of the voltage gradient, the dielectric constant, and the power factor.[350] Since both high voltage gradient and high dielectric constant are a necessity in capacitors, power factor is the only value which can be reduced. It has been shown that the dielectric losses in oil-impregnated papers depend upon the dielectric losses in the paper.[351]

Power factor and dielectric constant can be measured in an apparatus consisting of a conjugate Schering bridge, a source of alternating current, a three-stage amplifier for accurate detection of the null-balance point, and a test condenser and chamber.[352-354] The presence of metallic ions and the presence of lignin is associated with a high loss factor, the effect being greatest at high frequencies.[355]

Properties of Electrical Insulating Papers

All electrical insulating papers must meet high physical, chemical and electrical standards. Electrical papers meet their most severe tests in capacitor papers and in high voltage cable wrappings. In order to meet the strict requirements, most electrical insulating papers are made from kraft pulp, linen rags, cotton rags, or manila hemp.

The important physical properties of electrical insulation papers are thickness, density, finish, porosity, tensile strength, and tearing resistance.

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[346] D. O. Adams, *Paper Trade J. 122,* No. 7: 63–72 (Feb. 14, 1946)

[347] J. A. Van den Akker, *Paper Trade J. 119,* No. 26: 253–255 (Dec. 28, 1944)

[348] J. B. Whitehead, *Elec. Eng. 59:* 660–663T (Dec., 1940)

[349] F. M. Clark and V. M. Montsinger, *Gen. Elec. Rev.* 28: 286–290 (1925)

[350] H. H. Race, R. J. Hemphill and H. S. Endicott, *Paper Ind. 22,* No. 8: 792–798 (Nov., 1940)

[351] *Idem.*

[352] J. A. Van den Akker, *Paper Trade J. 119,* No. 26: 253–255 (Dec. 28, 1944)

[353] A. S. T. M. Tentative Method D 150–41T, D 150–42T (1941), Supplement to A. S. T. M. Standards, Part III 375–405

[354] C. R. Calkins, *Tappi 33,* No. 6: 278–285 (June, 1950)

[355] J. A. Van den Akker, *Paper Trade J. 119,* No. 26: 253–255 (Dec. 28, 1944)

Density, in particular, has an important effect on dielectric strength, dielectric loss, and dielectric constant. The true dielectric constant (K) of paper is related to density by the relationship which states that $(K-1)/(K+2)$ is proportional to density.[355]

The important chemical properties of electrical insulating papers are moisture content, ash, acidity, electrolyte content, and conducting particles.

Cellulose is a good insulator only so long as it is dry. An increase in moisture content brings an increase in the specific inductive capacity and power factor and a decrease in the dielectric strength.[356] The effect of moisture is particularly bad on dielectric loss (power factor).[357] It is desirable to keep the moisture content of insulating paper down to about 0.1%, but there is no advantage in going to a moisture content lower than this.[358] The low moisture content required in insulating papers makes it necessary to subject the paper to severe drying treatment. Ordinarily, the paper is heated under vacuum until the moisture reaches the required value. This results in some degradation of the paper. Ash generally varies from about 0.5 to 0.8% for condenser tissue, to about 1.0 to 3.0% for telephone wrapping paper and laminated insulation.[358]

An important property of insulating paper is the number of conducting particles in the paper. The presence of electrolytic materials, such as chloride ions left over from the bleaching operations, are especially deleterious, particularly in direct-current work. Because of this factor, papers bleached with hypochlorite are rarely used for electrical insulation. Conducting particles are measured by the number of electrical breakdowns when the paper is subjected to voltages somewhat lower than those obtained as the dielectric strength values.[359] In making the test on thin paper (papers under 0.0015 in. in thickness), the paper is placed between two metal electrodes, a flat metal plate and a smooth metal roller. The plate is connected to the grounded pole of a 110-volt current (a.c. or d.c.). The metal roller, a set of telephone receivers, and an 80,000-ohm resistor are connected in series, and the other terminal of the resistor is attached to the live pole of the 110-volt circuit. The number of conducting paths is taken as the number of clicks heard in the telephone headset when the roller is passed over the paper at a rate of 5 to 20 f.p.m. The results are reported as the number of clicks per square foot of paper. For thick paper (0.0015–0.030 in.), a somewhat different set-up is used, and the number of conducting paths taken as the total number of holes burned in the paper. The moisture content of the paper at the time of test must be no higher than 7%. The maximum number of tolerable conducting particles per square foot varies from less than 10 for dielectric capacitor paper to less than 0.01 for pressboards.[360]

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[356] C. Delevanti, Jr., and P. B. Hansen, *Paper Ind. 28:* No. 2: 288–289 (May, 1946)

[357] E. W. Greenfield, *J. Franklin Inst. 222:* 345–358 (1936)

[358] G. T. Kohman, *Ind. Eng. Chem. 31,* No. 7: 808–817 (July, 1939)

[359] Tests for Insulating Papers D202-48T, A. S. T. M. Standards on Paper and Paper Products, American Society for Testing Materials, 1916 Race St., Philadelphia 3, Pa.

Impregnated insulating papers are made by impregnating paper with paraffin, linseed oil, shellac, phenolic resins, chlorinated naphthalene, and chlorinated diphenyl.[361] Anthraquinone has been used as a chemical stabilizer,[362] and elemental sulfur has also been suggested for the same purpose.[363] It has been shown in many instances that the electrical properties of impregnated papers cannot be accurately estimated from the electrical properties of the paper and impregnant.

Types of Electrical Papers

Unimpregnated, impregnated, and vulcanized papers are among the types used in electrical insulation. Some of the most important electrical insulating papers are discussed below.

Condenser tissue[364] is a light-weight paper which is used in electrical capacitors for radio transmitters and receivers, and in telephonic equipment. This paper is made as thin as possible compatible with good electrical insulating properties. From the standpoint of high dielectric strength and life of the condenser, it is desirable to use several sheets of thin paper, rather than a single sheet of equivalent thickness. By using several thin sheets in place of a single thick sheet, the probability of failure due to imperfections is greatly reduced. The thickness of condenser paper varies from 0.0003 to 0.0015 in., and the weight from 4½ to 12 lb. (24 × 36—500). The finish, which is quite high, is obtained by supercalendering. High density is important in condenser tissue, because density is directly related to the dielectric strength of the paper and the capacity of the condenser. Highly porous papers are not suitable at all. The paper should be free of pin holes and conducting particles. Good condenser paper should have a low ash content, although the type of ash, rather than the amount, is of most significance. Soluble salts (measured by the specific conductivity of an aqueous extract of the paper) are particularly objectionable, chlorides being the most harmful. The paper should be as close to neutral as possible.

Most condenser tissue is made from linen, cotton, or sulfate pulp, or mixtures of these pulps. At one time, linen papers were used exclusively for capacitors, but linen papers have the disadvantage of gaining in power factor at temperatures greater than 70° C. Papers made from kraft pulp stand up better under heat and voltage.[365] The greater resistance of wood fibers may be due to the presence of natural anti-oxidants in kraft pulps.[366] Sulfite pulps are not so acceptable as kraft pulp because of the instability of the electrical and physical properties. It has been suggested[367] that the superior qualities of kraft pulp, as compared to bleached wood and linen pulps, for d.-c. units is due to the greater ion exchange ability of kraft pulps which causes the paper to adsorb hydrogen ions produced as a result of breakdown of the impregnant in the paper.

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[360] H. H. Race, R. J. Hemphill and H. S. Endicott, *Paper Ind. 22*, No. 8: 792–798 (Nov., 1940)

[361] D. A. McLean, L. Egerton and C. C. Houtz, *Ind. Eng. Chem. 38*, No. 11: 1111–1116 (Nov., 1946)

[362] D. A. McLean, U. S. 2,339,091 (Jan. 11, 1944)

[363] L. Egerton, U. S. 2,287,421 (June 23, 1942)

[364] Not to be confused with electrolytic condenser paper, which is a much heavier paper used in electrolytic condensers. It is made open and porous to pick up the maximum amount of electrolyte.

McLean[368] reports that controlled oxidation of kraft papers results in an improvement in insulation resistance, perhaps because of the immobilization of the ionic material through adsorption or chemical reaction. Calkins[369] found that the presence of carboxyl groups causes increased dielectric loss at higher temperatures. The source of excessive loss is evidently in the non-cellulosic constituents of the fiber, i.e., the lignin and the hemicelluloses.[369, 370] Miller and Hopkins[371] found, in the case of spruce kraft pulps, that the most critical factor is the hemicellulosic content. They obtained the lowest power factor at a hemicellulosic content in the neighborhood of 20%, but found that the ash content and tannin were also a factor. Delavanti and Hansen[372] found that acid washing and, to a lesser extent, water extraction are effective in reducing the power factor of kraft pulp.

Insulating tissue or coil-winding paper is a thin paper, ranging from 0.0005 to 0.003 in. in thickness, which is used for wire wrapping in transformers, radio wires, and magnet wires. The basis weight generally ranges from 5 to 30 lb. (24 × 36—500). The requirements are largely the same as those for capacitor paper. The paper must not contain corrosive materials which will attack fine copper wire.

Cable paper is strong paper which is used in the winding of high- and low-voltage cables, and in transformers, coils, and magnets. The paper is generally applied spirally in the form of strips. Winding is done by machine at high speed and high tension so that paper having high machine direction tensile strength and stretch, and high cross direction tear is required. Winding is often done under controlled humidity conditions. The paper is relatively heavy and generally has a basis weight between 50 to 125 lb. (24 × 36—500). Paper made from manila hemp has long been considered the standard because of the high strength requirement, but kraft and mixed kraft and hemp papers have been used. The paper must be free of pin holes, and must not contain conducting particles (e.g., iron). High dielectric strength is, of course, very important in cable papers. Dielectric losses are also an important consideration.

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[365] D. A. McLean, L. Egerton, G. T. Kohman and M. Brotherton, *Ind. Eng. Chem. 34,* No. 1: 101–108 (Jan., 1942)

[366] D. A. McLean, U. S. 2,339,091 (Jan. 11, 1944)

[367] D. A. McLean, L. Egerton, G. T. Kohman and M. Brotherton, *Ind. Eng. Chem. 34,* No. 1: 101–109 (Jan., 1942)

[368] D. A. McLean, *Ind. Eng. Chem. 39,* No. 11: 1457–1461 (Nov., 1947)

[369] C. R. Calkins, *Tappi 33,* No. 6: 278–285 (June, 1950)

[370] C. C. Delevanti, J., and P. B. Hansen, *Paper Trade J. 121,* No. 26: 241–249 (Dec. 27, 1945)

[371] H. F. Miller and R. J. Hopkins, *Gen. Elec. Rev. 50,* No. 12: 20–24 (1947)

[372] C. Delevanti, Jr., and P. B. Hansen, *Paper Trade J. 121,* No. 26: 241–249 (Dec. 27, 1945)

Pressboards made on a wet machine in thicknesses ranging from 0.005 to 0.125 in. are used as a spacing and insulating medium in electrical equipment. The stock used is generally rag or mixtures of rag and kraft. Vulcanized fiber is used for electrical insulation in winding motor armatures. The desirable features of vulcanized fiber are good mechanical strength and high dielectric strength. Certain grades of low caliper are known as fish paper.

A special type of electrical paper is that used in certain recording instruments. This paper must have a high conductivity and consequently is filled with 50% or more of carbon black.

Microscopical Analysis

In addition to the chemical, physical, and optical tests commonly made on paper, it is possible to obtain considerable information about the properties of paper by examination with a microscope. Among the important uses of the microscope in paper mill work are those for fiber length analysis, determination of fiber species, dirt and speck analysis, determination of amount of fiber treatment, study of rosin and starch sizing, and examination of paper for fillers.

The value of a microscope examination depends to a large extent upon the skill of the microscopist and his ability to relate his observations to practical application. The value of the microscope has been mentioned at frequent intervals throughout this book. Its use for identifying fibers and measuring the length of fibers has already been mentioned. The following sections are concerned with the identification of fibers according to the process by which they were pulped and purified. Dirt and speck analysis and other special uses of the microscope are also discussed in this section.

Types of Microscopes

There are several types: the optical microscope, the ultramicroscope, and the electron microscope. For the examination of the crystalline structure of materials, x-ray analysis is very valuable.

The resolving power of the optical microscope is limited to objects no closer together than the wavelength of light. Even with the best models it is impossible to increase resolution beyond 1000 × to 1400 ×, which means that it is impossible to resolve objects less than 0.2 micron in size. When the object is less than about 0.5 micron (0.0005 mm.) in diameter, the image is not a true geometrical outline of the particle, and this lack of outline becomes worse the smaller the particle, down to a size of about 0.1 micron, where the object completely vanishes from view.

In spite of the above limitations, the optical microscope has considerable value in the paper industry where it is widely used for dirt speck analysis, for fiber measurement, for determining the degree of beating, and for making fiber analysis.

The ultramicroscope can be used to investigate particles smaller than those which are visible in the optical microscope. The "slit" ultramicroscope consists of an ordinary optical microscope in which a slit of light is used at right angles to the microscope to illuminate the particles by scattering the light and making them visible as spots of light against a dark background. The ultramicroscope shows up particles as small as 5 millimicrons, and with special refinements, as low as 3 millimicrons. Particles which are not visible in the ultramicroscope are called ultramicroscopic particles and are considered to be in true solution. The ultramicroscope is sometimes used to count the number of particles present in a colloidal dispersion. The size of the particles can be determined from the mass of the dispersed phase (obtained by evaporation or filtration) and the number of particles in the dispersed phase (determined in the ultramicroscope).

The electron microscope is a newer instrument which uses a stream of electrons in place of ordinary light. In the electron microscope, pictures can be taken which later can be enlarged to show useful information at ca. 50,000 × to 100,000 ×. The advantage of the electron microscope over the ordinary optical microscope lies in its improved resolving power, and the fact that its ultimate resolution does not decrease appreciably with an increase in magnification. It has a resolving power down to 0.01 to 0.004 micron, and promises to be effective down to 7 A. It has a depth of focus of 7.0 microns at its greatest resolution. The electron microscope is of great value in studying the problems of pulp and paper manufacture because it permits study of materials which are not visible in either the optical or ultramicroscope.

Like ordinary visible light, x-rays are electromagnetic radiations. They differ from light in having a very much shorter wavelength, being approximately 10^{-8} cm. or 1 angstrom unit (A.) in length, compared with about 10^{-4} cm. for light. These rays are much more penetrating than electron beams and are diffracted by atomic planes deep within the crystal, whereas the electrons in the electron microscope are diffracted mostly by planes lying near the surface. X-ray photographs can be taken by means of special photographic film. Considerable experience is necessary in order to interpret the results, but in the hands of a competent physical chemist, they shed considerable light on the configuration of crystalline materials.

Types of Fiber Stains

The use of stains for the identification of different fibers became of importance after the introduction of wood fibers in papermaking. When only rag fibers were used, there was no necessity of determining fiber composition, but after the introduction of straw and wood pulps, it became essential to find some means of distinguishing between wood, straw, and rag fibers. Later, as the number of different wood pulps increased, it became necessary to find a means of distinguishing between groundwood, soda, bleached and unbleached sulfite, and bleached and unbleached sulfate. Satisfactory stains have been developed for distinguishing between these wood pulps, but the problems of identification are becoming greater all the time because of a broadening in the types of papermaking fibers and because of special methods of pulping and bleaching. Some of the relatively new pulps having different characteristics are hardwood sulfite, bleached groundwood, and semichemical pulp.

Fiber analysis is important for a number of reasons. It furnishes a means by which the mill chemist can check on current pulp production. It is useful for analyzing old papers purchased as a source of pulp. It is a means for analyzing competitive papers. Fiber analysis is useful in setting up specifications on a given grade of paper and checking on whether the specification has been met. Thus, in the manufacture of rag content papers, a fiber analysis showing the percentages of rag and sulfite fibers serves as a check for both the mill and the purchaser to see that the paper has met specifications. A fiber analysis gives information on what may be expected in permanence and performance of the paper. Bond and ledger papers are sometimes specially watermarked to show the rag content. In the case of papers for the U. S. Government Printing Office, watermark consists of the seal of the United States with a halo of stars, the number of which depends upon the rag content. Thus, one star signifies 25% rag, two stars signifies 50% rag, three stars 75% rag, and four stars 100% rag. Chemical wood papers for the U. S. Government Printing Office are not watermarked.

Preparation of Specimen

In preparing the specimen for staining, it must first be reduced to the fibrous state. The sample may be either a pulp, a highly sized paper, an impregnated paper, or a specially treated paper. Pulps are readily broken up in water, with the exception of groundwood, which must be given special treatment.

Rosin-sized papers should be torn into small pieces, placed in a small beaker, and boiled in a 1% sodium hydroxide solution to remove the size. After boiling, the liquor should be decanted and the sample washed with distilled water, covered with 0.05 *N* hydrochloric acid, and then washed again in distilled water. If the specimen contains wool fibers, the caustic treatment must be eliminated.

Impregnated or coated papers must be given special treatment. Asphalt- or tar-treated papers can be digested in heavy or medium coal tar oil on a steam bath for one hour and later extracted with benzene to remove the asphalt. The digestion in oil may have to be repeated one or more times before extracting with benzene. Waxed papers can be Soxhlet-extracted with ether, alcohol, ethyl acetate, or acetone to remove the wax. Rubber-treated papers can be Soxhlet-extracted with chloroform, dichlorobenzene, nitroanisole, isopropylbenzene (cumen), or similar solvents to remove the rubber.[373, 374] The sample should then be boiled in a very dilute solution of wetting agent. Parchment papers can be broken up by soaking in acid (either concentrated HCl or a mixture of 50 parts of water and 50 parts concentrated H_2SO_4) until the paper starts to break up. The action of the acid should then be stopped immediately by diluting in water or by neutralizing with NaOH.[374] Viscose-treated papers can be disintegrated in hot calcium nitrate solution.[375] Coated papers can be prepared by soaking in a suitable solvent and then rubbing the coating loose with a special abrasion device. Dyes can be removed by treatment of the paper with bleach liquor, nitric acid, alcohol, ammonia, hydrochloric acid, hydrosulfite, or similar reagents, depending upon the type of dyestuff present. Melamine-treated wet strength papers can be defibered with the aid of hydroxylamine hydrogen chloride.

After the sizing or impregnating agent has been removed, a small amount of the wetted sample is rolled in a small ball between the fingers until the fibers are thoroughly loosened (chewing in the mouth is sometimes used as a method with samples containing groundwood). Next, the small pellet of pulp should be placed in a large test tube and shaken with a small amount of water. In some cases, about 10 to 12 glass beads may be added to help in breaking up the fiber bundles, but shaking should not be so severe that the fibers are disintegrated. Water should be added gradually with repeated shakings to obtain a fiber concentration of about 0.05 to

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[373] J. H. Graff, *Pulp and Paper Microscopy,* The Institute of Paper Chemistry, Appleton, Wisconsin (1942)

[374] TAPPI Standards

[375] J. H. Graff, *Pulp and Paper Microscopy,* The Institute of Paper Chemistry, Appleton, Wisconsin (1942)

0.1%. The fibers are now ready to be transferred to a microscope slide for staining.

Preparation of the Slide

There are many techniques for preparing microscope slides for staining and counting. In the TAPPI method, the fibers are transferred to the slide by means of a dropper consisting of a glass tube (15 cm. long and 6 mm. internal diameter) with one end fitted with a rubber bulb and the other end carefully smoothed, but not constricted. After the fibers are thoroughly mixed in water, the dropper should be inserted into the fiber suspension 5 cm. below the surface, two bubbles of air expelled, and the tube filled to a distance of about 13 mm. The entire contents of the tube should then be transferred to the slide, making 4 drops in all. This is repeated until the slide is uniformly covered with drops. A metal dissecting needle can be used for spreading the fiber suspension evenly over the slide, after which the water is evaporated by heating the slide in an oven or on a hot plate where surface temperature is about 50 to 60° C. Tapping the slide with the point of the dissecting needle during drying helps to maintain uniform distribution of the fibers. The slide should be left until it is completely dry, and should not be touched with the fingers. In a properly prepared slide, the fibers should be evenly distributed at a low density on the slide so that individual fibers can be examined. If the fibers are too dense, the stain will not take properly and the fibers will be difficult to count. Some chemists prefer to draw a line on the slide 1 in. from each edge, using aluminum stearate dissolved in benzene to keep the fibers on the slide.

One of the most important considerations in the preparation of microscope slides for fiber analysis is the matter of cleanliness. All slides and cover glasses should be thoroughly washed with soap, rinsed in distilled water, and kept in 50% alcohol. The slides should be polished with clean cheesecloth before using. Unless the slides are perfectly clean, the fiber suspension will no spread evenly and there will be a tendency for iodine (in iodine-base stains) to precipitate around the dirt specks.

When the slide and fibers are thoroughly dried and cooled, the fibers are ready for staining. The methods of applying stains vary according to the type of stain used. In applying iodine base stains, the stain is added to the fibers, a cover glass is applied, and the stain is allowed to stand on the fibers for one to two minutes. The excess stain can then be removed by pressing the slide gently between two blotters or by tilting the slide against a piece of filter paper.

There are a large number of stains available to the paper chemist. Graff[375] lists the following stains as being useful:

(*1*) Stains for determining groundwood or woody fibers in paper, e.g., phloroglucinol and aniline sulfate.

(*2*) Iodine-metallic salt stains for differentiating between groundwood, chemical wood, and rag pulps, e.g., Herzberg stain and "C" stain.

(*3*) Dye-base stains for determining the degree of cooking, bleaching, and purity of the fibers, and for the purpose of differentiating between unbleached sulfite and unbleached sulfate pulps, e.g., Kantrowitz-Simmons, and Lofton-Merritt.

(*4*) Special stains for positive identification of jute, manila, flax, hemp, and other special fibers.

(*5*) Stains for determining the amount and type of sizing and coating on paper.

In preparing all stains, chemically pure reagents should be used and the dry ingredients should be carefully weighed on an analytical balance. The liquid fraction should be carefully measured volumetrically. In making up concentrated salt solutions used in the stain, a Westphal balance generally gives best results. Distilled water should be used both for preparing the stains and for preparing the fiber suspensions, since tap water contains enough dissolved inorganic matter and is often so alkaline that it throws off the color reaction. Stains must sometimes be adjusted after they are made in order to obtain the correct color reactions, and for this purpose standard pulps should be kept on hand. Color charts are available for certain stains to indicate the color reactions to be expected on different fibers, but these charts are often confusing unless the observer has had considerable experience.

Examination of the Slide

The light used for examining the slides is very important and should be kept constant during the period of the examination. Once the condenser on the microscope has been set, it should not be changed. North daylight is best, but when this is not avaliable, special daylight lamps can be used with good results. A daylight fluorescent lamp placed about 10 to 12 in. from the mirror of the microscope has the advantage of furnishing a constant source of acceptable light.

One fact which is well known to anyone who has used fiber stains is that it is impossible to ascribe any positive color to the stained fibers. This is due to the fact that different batches of stains vary slightly in their staining properties and, more importantly, because different pulps vary in their degree of cooking and bleaching. Hard, medium, and soft pulps have quite different staining reactions, as would be expected from the differences in the amount of lignin and other impurities which they contain. Even the various fibers from the same cook will sometimes show quite different staining characteristics, particularly unbleached fibers cooked by the sulfite process.

Methods of Counting

The percentage of different fibers in an unknown sample can be determined by the estimation method or by the dot count method. In the estimation method, an estimate is made of the relative proportion of different fibers in the microscope field. This method is fairly accurate in the hands of an expert, but requires considerable experience. It is losing favor among chemists.

In the dot count method, each individual fiber is counted as it passes under the intersection of two crosshairs on the eyepiece. A mechanical stage is used for moving the slide in a straight line across the field. Each fiber is counted once every time it passes under the crosshair, regardless of whether it has been counted before. However, if a single fiber remains under the crosshair intersection for a considerable part of its length, it should be counted only once. All material which is longer than it is wide should be considered as a fiber or as a fiber fragment. Fiber fragments should be given a value according to their relationship to the full fiber length. In samples containing groundwood, there will be a considerable number of fiber fragments in the groundwood portion. These fragments should be ignored if they are no longer than they are wide, but if they are slightly longer than they are wide, they should be counted as one-quarter to one-sixth of a fiber. All other parts of groundwood should be counted as single fibers. In the case of fiber bundles, each fiber in the bundle should be counted separately.

In making a fiber count, it is customary to count three lines horizontally and two lines vertically on each slide so that the area of the slide is well covered. Some analysts prefer to count five lines horizontally, omitting the vertical counts. As a rule, only one type of fiber is counted each trip across the field, and the second fiber is then counted on the return trip along the same line. Some analysts, however, prefer to count all fibers in a single trip across the field, which is probably the most accurate method when there is a sharp difference between the fibers. If the fibers are hard to differentiate, the best method is to count the fiber with the most obvious color on the first trip and then count the total number of fibers on the return trip, subtracting the two readings to obtain the number of the second fiber type. A total of at least 400 to 600 fibers should be counted for each unknown sample. When a fiber count is properly carried out, the per cent error from the true average of the fiber composition should be less than 2 to 3%.[376]

Use of Weight Factors

Fiber counting in the above fashion gives the percentage by number of each type of fiber in the unknown sample. However, the papermaker handles pulp by weight, and it is therefore necessary to convert the results into percentage by weight. Weight factors are used for this purpose. In reporting results, it should be clearly stated whether the report is in percentage by number or percentage by weight.

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[376] J. H. Graff, *Paper Trade J. 101*, No. 2: 14–28 (July 11, 1935)

Weight factors are necessary for converting from percentage by number to percentage by weight, because all fibers do not weigh the same, as shown in Table XXXIX.[377] For example, in an equal weight of soda and rag pulp, there will be twice as many soda fibers as rag fibers. Since rag fibers are taken as the basis of comparison, the weight factors for these two pulps are therefore 1.0 for rag and 0.5 for soda fibers. The weight factors generally used for the different commercial pulps are listed in Table XL. Weight factors are ordinarily not affected by bleaching or by the degree of beating. Isenberg and Peckham[377a] found that cotton linters had a

TABLE XXXIX

AVERAGE NUMBERS OF FIBERS PER GRAM OF PULP
Probable error ± 5,000

Pulp	Number of fibers
Rag	8,550,000
Softwood U. B. sulfite	9,250,000
Softwood B. sulfite	9,880,000
Softwood U. S. western sulfite	6,800,000
Softwood B. western sulfite	7,050,000
Softwood U. B. kraft	9,525,000
Softwood B. kraft	9,225,000
Softwood U. B. southern kraft	5,500,000

TABLE XL

WEIGHT FACTORS FOR CONVERTING FROM PERCENTAGE BY NUMBER TO PERCENTAGE BY WEIGHT

Pulp	Factor
Rag	1.00
Sulfite (spruce)	0.90
Sulfite (western hemlock)	1.20–1.23
Sulfite (hardwoods)	0.60
Kraft (eastern U. S.)	0.90
Kraft (southern pine)	1.55
Kraft (hardwoods)	0.70
Soda (hardwoods)	0.50
Groundwood (softwoods)	1.30
Straw and bast fibers	0.55

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[377] J. H. Graff, M. A. Schlosser and E. K. Nihlen, *Tech. Assoc. Papers 24:* 529–531 (June, 1941)

[377a] I. H. Isenberg and C. L. Peckham, *Tappi 33,* No. 10: 527, 528 (Oct., 1950)

different weight factor from regular rag pulp, and that the weight factor varied in the case of second cut linters from 1.50 to about 1.05 when the freeness due to beating was changed from 850 to 450 (S.R.).

Iodine Stains

Staining is a colloidal phenomenon. Most of the staining reactions are based upon the fact that lignin has an affinity for certain salts and basic dyes, that hemicelluloses have an affinity for iodine, and that cellulose has an affinity for direct dyes. The blue color obtained upon the addition of an iodine stain to a bleached pulp is due to the adsorption of iodine by the hemicellulose in the pulp (in the same way that starch is stained blue with iodine). Zinc chloride in the stain increases the hydration of the hemicellulose, resulting in greater iodine adsorption, and hence intensifies the blue color. Highly lignified fibers, on the other hand, are stained yellow rather than blue because lignin has no readily available hydroxyl groups to adsorb the iodine in a definite pattern, and because the lignin prevents the zinc chloride from swelling the hemicellulosic material in the fibers.

The amount of iodine adsorption by the fibers is in direct relationship to the moisture content of the fibers, and consequently the fibers should be thoroughly dried before staining.[378] In all iodine stains, the color reaction, in going from an uncooked pulp, to a cooked pulp, to a completely purified pulp, is from yellow, to blue, to red. Thus, with iodine base stains, groundwood fibers stain yellow, chemical wood fibers stain blue, and rag fibers stain a wine red. The iodine stains include the Herzberg stain, Sutermeister's stain, Selleger's reagent, the Graff "C" stain, Wilson's stain, and Laughlin's stain. These stains are discussed in the following sections.

Herzberg Stain. One of the most important of the iodine stains is the Herzberg stain. This stain is useful for differentiating between rag, groundwood, and chemical wood pulps as a class, but cannot be used by the average observer for differentiating between the various chemical wood pulps. The wide usage of this stain is due to its ease of preparation and its traditional use in the paper industry.

The color reactions obtained with the Herzberg stain depend upon the amount of lignin and hemicellulose in the fibers. Heavily lignified fibers such as groundwood, uncooked manila hemp, raw straw, and jute stain yellow. Highly purified fibers such as cotton and linen rag pulp and bleached manila hemp stain a purplish pink to a wine red color. Most cooked and bleached sulfite and soda pulps stain a blue color, although there is a tendency toward a reddish purple in the case of the highly purified grades, and a tendency toward an olive gray in the case of the raw grades.

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[378] F. L. Minnear and J. R. Withrow, *Paper Trade J. 91,* No. 24: 51–55 (Dec. 11, 1930)

Hardwood soda fibers stain a deeper blue than softwood sulfite fibers because of their thicker fiber walls. Of the synthetic fibers, vinyon is left uncolored by Herzberg stain, whereas cellulose acetate fibers are stained yellow and viscose fibers are stained a deep blue or violet.

If sufficient care is used in making the Herzberg stain, it should be satisfactory as originally prepared. However, it is sometimes necessary to adjust the stain. If the stain produces too weak a blue on chemical pulps, additional zinc chloride should be added. If the red and yellow colors are weak, additional iodine can be added. The addition of water tends to weaken the predominating color. Some analysts prefer to keep several lots of stain on hand which have been specially adjusted so that they work best on certain fiber combinations. A stain which works well on groundwood and unbleached sulfite does not work well on rag and bleached sulfite or soda.

There have been many variations in the preparation of the stain which is now generally known as the Herzberg stain. The standard method of preparing Herzberg stain, as accepted by TAPPI, is as follows:

Solution A: 40 cc. of zinc chloride solution of 1.80 specific gravity at 28° C. This solution can be made by adding about 25 cc. of distilled water to 50 g. of cp. anhydrous zinc chloride sticks.

Solution B: 5.25 g. of dry potassium iodide and 0.25 g. of dry iodine in 12.5 cc. of distilled water. (Mix the dry ingredients together and add water, drop by drop.)

Add solution *B* to solution *A* and, after mixing thoroughly, pour the solution into a tall narrow cylinder and allow to stand until the precipitate has settled. The clear solution is then pipetted into a dark bottle and a leaf of iodine added. The stain should be renewed every month or so.

In using the Herzberg stain, a few drops of the stain are added to the dry fibers on the slide, a cover glass placed over the fibers, and the stain is left for at least one minute. At the end of this time, the excess stain is removed by pressing the slide and cover glass between two blotters, or by tilting the long edge of the slide into contact with a blotter.

The Graff "C" Stain. Graff has developed a series of iodine stains which are improvements on older iodine stains. The most important of these is the "C" stain. In using the "C" stain, between two and three drops of the stain should be added to the dry fibers on the slide and the slide covered with a watch glass. After standing exactly two minutes, the excess stain should be removed by pressing the slide between blotters or by tilting one edge against a blotter.

The "C" stain is made by combining potassium iodide-iodine solution with definite amounts of metallic salts. It is prepared as follows:

To 20 cc. of standard aluminum chloride solution (1.15 specific gravity at 28° C.), 10 cc. of calcium chloride solution (1.36 specific gravity at 28° C.) and 10 cc. zinc chloride solution (1.80 specific gravity at 28° C.), add 12.55 cc. of iodine solution made by adding 50 cc. of distilled water to 0.9 g. of dry potassium iodide and 0.65 g. dry iodine. After mixing well, the solution should be poured into a tall narrow vessel and placed in the dark for 12 to 24 hours. At the end of this period, the clear portion is pipetted into a dark, glass-stoppered dropping bottle and a leaf of iodine added. The stain should be kept in a dark cool place when not in use.

The "C" stain differentiates between a wide variety of fibers, including raw, medium, fully cooked, and bleached softwood sulfite pulps and raw, medium, well-cooked, and bleached softwood sulfate pulps. The stain also can be used to distinguish between softwood and hardwood pulps, hardwood kraft, sulfite, alpha, and soda pulps, as well as jute, manila, hemp, and straw pulps. In order to be able to differentiate between all these various fibers, considerable experience is necessary, but in the hands of an experienced observer, the "C" stain is extremely useful.

One of the most difficult jobs in fiber analysis is differentiating between bleached sulfite and bleached sulfate, but this can be done fairly well by the "C" stain; under the "C" stain, bleached sulfite fibers stain a light reddish to pinkish blue (vinaceous fawn), whereas bleached sulfate fibers stain a darker blue which may have some red (violet plumbeous).

Differentiation with the "C" stain should not be made on the basis of color alone, since the depth of color and clarity of the color are equally important, particularly in the case of unbleached pulps. For example, with a given specimen of unbleached sulfite pulp, the "C" stain is likely to produce colors ranging from yellow, to a light tan, to a gray, almost colorless, fiber, depending upon the degree of purification of the individual fibers. It is possible to obtain an approximate indication of the bleachability of a sulfite pulp by counting the number of undercooked (yellow) fibers in the specimen. Unbleached sulfate pulps also show considerable variation in color in the same sample. The range of colors is very much the same as that shown by unbleached sulfite, but whereas the colors with unbleached sulfite are light and clear, the colors obtained with unbleached sulfate are muddier and much darker. Bleached fibers do not show as wide variation in color as unbleached fibers because of the greater uniformity of the bleaching action.

The colors developed by the "C" stain on different pulps are given in Table XLI. However, it should be pointed out that these are only approximate colors, and each observer must make his own interpretations based upon examinations of known pulp samples. Color charts are available for the "C" stain, and these are helpful in becoming familiar with this stain.

TABLE XLI

Colors Developed by Graff "C" Stain

Groundwood
  Vivid yellowish orange
Rag
  Red to reddish orange
Manila
  Light yellowish green (raw)
Jute
  Yellowish orange (unbleached)
  Light yellow-green (bleached)
Straw, Bamboo, Cane, etc.
  Light yellow to weak greenish yellow (raw)
  Greenish gray to bluish gray (unbleached and bleached)
Sulfite Coniferous Pulps
  Generally yellow to gray
  (A) Softwood unbleached sulfite
    Yellow, cartridge buff
  (B) Softwood lightly bleached sulfite
    Pale vinaceous fawn
  (C) Softwood eastern American and European bleached sulfite
    Pallid purple drab
    Very light vinaceous gray
  (D) Softwood West Coast bleached sulfite
    Pale purplish vinaceous
Softwood alpha pulps
  Pale brown to pink and red
  (A) Softwood unbleached alpha
    Cinnamon buff
  (B) Softwood lightly bleached alpha
    Light purplish lilac
  (C) Softwood bleached alphas
    Light corinthian pink
    Light pinkish vinaceous
    Light vinaceous Congo pink
Softwood sulfate pulps
  Greenish yellow to dark bluish gray
  (A) Softwood unbleached sulfate
    Mineral gray
    Ecru drab
  (B) Softwood bleached sulfate
    Pale violet plumbeous
    Glaucous gray
  (C) Softwood refined sulfate
    Deep vinaceous lavender
    Pale vinaceous lilac
Hardwood sulfite pulps
  Pale yellow-green to purplish blue

TABLE XLI (*continued*)

(A) Hardwood bleached sulfite
    Very light grayish blue violet
    Very pale windsor blue
    Pale grayish vinaceous
    Pale purplish vinaceous
Hardwood alpha pulps
  Reddish orange to dusky red
  (A) Hardwood alphas
    Pinkish vinaceous
    Etruscan red
    Light vinaceous Congo pink
    Light vinaceous
Hardwood soda pulps
  Blue-green to blue, Russian blue
Hardwood sulfate pulps
  Blue-green to blue
  (A) Hardwood unbleached sulfate
    Light vinaceous purple
    Orient blue
  (B) Hardwood bleached sulfate
    Alice blue
  (C) Hardwood refined sulfate
    Deep vinaceous lavender
    Alice blue

Sutermeister "A" Stain. There are two Sutermeister stains, both of which belong to the class of iodine stains. The original Sutermeister stain was applied in two stages, but Graff[379] modified the stain to a one-solution stain which he called the "A" stain. The "A" stain is prepared as follows:

Solution A: Calcium chloride solution of 1.36 specific gravity at 28° C. is prepared by adding about 100 g. of cp. calcium chloride to 150 cc. of distilled water.

Solution B: Prepared by adding 50 cc. of distilled water to a mixture of 0.9 g. of dry potassium iodide and 0.65 g. of dry iodine.

Add 5 cc. of solution *B* to 45 cc. of solution *A* and, after mixing well, pour the mixture into a dark glass-stoppered bottle. Add a leaf of iodine and keep in the dark when not in use.

The colors developed by this stain are as follows;

Red or brownish red—cotton, linen, hemp, ramie
Dark blue—bleached soda (from hardwoods)
Bluish or reddish violet—bleached sulfite and thoroughly cooked unbleached sulfite.
Greenish—jute, manila hemp, and the more lignified fibers in unbleached sulfite.

Wilson Stain. One of the newer iodine stains is the Wilson stain. This stain has several advantages over the older iodine stains, among which are greater ease of preparation, less overlapping of colors, and more uniform coloring on any one type of pulp. The Wilson stain is prepared as follows:[380]

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[379] J. H. Graff, *Paper Trade J. 100,* No. 16: 45–50 (Apr. 18, 1935)

Iodine crystals cp.	0.8 g.
Cadmium iodide cp.	35.0 g.
Distilled water	50.00 cc.

Heat the above to 110° F. and break the iodine crystals with the end of a stirring rod. Decant the solution from one beaker to another to observe the point where no dissolved solids remain. Then add the following in order, stirring:

Distilled water	90 cc.
Formaldehyde	7 cc.
Calcium nitrate cp., $Ca(NO_3)_2 4H_2O$	70 g.
Cadmium chloride cp., $CdCl_2 2.5H_2O$	20 g.

Formaldehyde has a stabilizing action and tends to improve the brilliancy of the colors.

In using Wilson stain, a few drops of stain are placed on the dry fibers on the slide, a cover glass applied, and after about ten seconds, the excess stain removed from the edges of the slide with a blotter. The slide may be examined at once. Some of the colors developed are as follows:

Soda—purple
Linen and rag—pink
Kraft—brown (some gray)
Unbleached sulfite—colorless
Bleached sulfite—lavender
Bleached sulfate—blue
Cotton—red
Groundwood—yellow
Straw—predominately green

This stain is particularly useful for distinguishing between unbleached sulfite and unbleached sulfate fibers.

Modified Selleger Reagent. Selleger's reagent is an iodine stain which is particularly useful for distinguishing soda (hardwoods), cooked straw, and esparto fibers, since these fibers stain a distinct blue, whereas most other fibers have a pale rose or yellow color.

There are two methods for making Selleger's reagent, and these are described below:

Method I: Dissolve 100 g. of calcium nitrate in 50 cc. water. Add 3 cc. of KI solution, made by dissolving 8 g. of KI in 90 cc. of water. Add 1 g. of iodine and let stand for one week.

Method II: Dissolve 0.267 g. of potassium iodine in 50 cc. of water. Add 1 g. of iodine and let stand 2 weeks, shaking each day. Then dissolve in this solution 100 g. of calcium nitrate. The stain is then ready for use.

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[380] N. F. Wilson, *Paper Ind. 27,* No. 2: 215–216 (May, 1945)

The colors produced by Selleger's reagent are as follows:

Bleached coniferous woods—light rose
Unbleached coniferous woods—clear yellow
Poplar and birch—violet blue
Esparto and cooked straw—blue
Manila and hemp—wine red
Linen and cotton—rose-brownish
Groundwood, jute, uncooked straw—deep yellow

The stain is good for about two to three months.

Laughlin Stain. A special stain for differentiating between bleached sulfite and bleached sulfate fibers has been introduced by Laughlin[381] and elaborated upon by Stocker and Durant.[382] This stain is prepared as follows:

Solution A (basic orange stain): 0.7 g. Dupont Basic Orange 3RN, 50 ml. distilled water, 50 ml. 95% ethyl alcohol. The dye is dissolved in the water and then the alcohol added.

Solution B (dilute hydrochloric acid, approximately 0.02 *N*).

Solution C (regular Herzberg iodine stain).

Solution D (chloride stain): 50 g. zinc chloride (fused sticks), 15 g. calcium chloride (anhydrous).

Make up to a volume of 100 ml. with distilled water and add 0.5 ml. 0.02 *N* hydrochloric acid.

It is not advisable to keep the solution for a period exceeding two months.

The method of using this stain is as follows. A representative sample of the unknown is boiled in acidified water (4 drops of concentrated hydrochloric acid to 50 ml. of distilled water) for about one hour. The acidified water is decanted and replaced with distilled water, after which the sample is again brought to a boil. The sample is swirled around in a flask containing a few glass beads until it is well dispersed. The sample is diluted to the proper consistency and slides prepared. Enough of solution *A* is then added to cover the fiber (approximately 0.5 ml.). This is allowed to stand on the fibers for one minute, after which the slide is blotted with a clean filter paper and rinsed once with solution *B*, and then blotted dry. Enough of solution *C* is added to cover fibers (approximately 0.5 ml.), allowed to stand thirty seconds, and then the slide is blotted. Finally, one drop of solution *D* is added and the cover glass immediately placed on the slide. After one minute, the colors develop and the slide is ready for examination. Differentiation is difficult after a period of thirty minutes, as there is a definite fading of color.

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[381] E. R. Laughlin, Canadian Industries, Ltd. Report on Fiber Analysis Methods. (June, 1938)

[382] F. W. Stocker and L. G. Durant, *Pulp Paper Mag. Canada 46:* 67–69 (Apr., 1946)

The results obtained in using this stain are summarized below:

Pulp	Colors observed
Acid cooks	
Unbleached sulfite	Medium to dark amber
Bleached sulfite (approx. 80 G.E. brightness)	Pale tan
High bleached sulfite (approx. 90 G.E. brightness)	Will stain a very pale blue which fades out in one to two minutes to a pale tan.
High alpha bleached sulfite	Will stain a very pale blue which fades out in one to two minutes to pale tan. Practically unstained.
Alkaline cooks	
Unbleached kraft	Dirty gray to khaki, some blue
Regular bleached kraft	Medium blue
High alpha bleached kraft	Pale to medium blue
Bleached soda	Deep to medium blue

Dye-Base Stains

Several stains use dyestuffs as their main base. In these stains, dyes are taken up by the fibers according to complicated relationships between the purity (lignin content) of the fibers and the dyeing properties of the dyestuff. These stains are used principally for determining the extent of cooking and extent of bleaching of the fibers. Some of the important dye-base stains are described below.

Bright Stain. The Bright stain is used for differentiating between bleached and unbleached pulps, and for indicating the approximate degree of cooking. The stain consists of three solutions, which are made as follows:

Solution A: 2.70 g. cp. $FeCl_3 \cdot 6H_2O$ in 100 ml. distilled water.

Solution B: 3.29 g. cp. potassium ferricyanide ($K_3Fe(CN)_6$) in 100 ml. of distilled water.

Solution C: 0.50 g. benzopurpurine (Dupont Purpurine 4B conc.) in 100 ml. of 50% ethyl alcohol. The solution must be warm to keep the dye in solution.

Solutions *A* and *B* should be filtered every day just before use.

In using this stain, a small amount of pulp (1.5 g.) is placed in a 50-ml. beaker containing equal parts of solutions *A* and *B* and stirred for one minute. The pulp is then screened, squeezed dry, and washed by shaking in about 500 ml. of distilled water. The sample is again screened and squeezed dry, after which it is placed in 50 ml. of solution *C* and warmed gently for about two minutes. The pulp is again screened, squeezed dry, and washed in 500 ml. of distilled water, after which slides are prepared.

The lignin in partially cooked, unbleached fibers reduces the ferric-ferricyanide to Prussian blue, which is taken up by the unbleached fibers.

Bleached fibers, on the other hand, contain no lignin and hence do not take up a blue color, but absorb benzopurpurine in the subsequent stage, thus taking on a red color. Unbleached fibers vary in color from blue to red, depending upon the degree of cooking. The colors developed[383] are as follows: 20% cooked, light to dark blue; 40% cooked, light bluish gray; 60% cooked, blue-gray with purplish pink markings; 80% cooked, strong purplish pink; 100% cooked, red. Graff[383] has shown that the number of red fibers in unbleached sulfite pulp increases almost directly with a decrease in the permanganate number.

Kantrowitz-Simmons Stain. One of the most useful modifications of the Bright stain is the Kantrowitz-Simmons stain. This stain can be used to differentiate between groundwood and unbleached fibers on one hand, and bleached fibers on the other. The solutions used are the same as those in the Bright stain.

In using the Kantrowitz-Simmons stain, three drops of solutions *A* and *B* are added to the fibers on the slide and allowed to remain one minute. The excess solution is then removed by blotting with filter paper, a few drops of solution *C* are added, the specimen is covered with a cover glass and left for two minutes. The excess stain can then be removed by carefully washing with distilled water, playing the water gently at one edge of the cover glass. Too much washing removes the red color.

The color reactions obtained with the Kantrowitz-Simmons stain are as follows: red, bleached sulfite, soda, sulfate, and rag; blue, unbleached sulfite, sulfate, groundwood, and jute. Ordinarily, this stain is quite reliable, but care must be exercised in the staining technique to obtain the true color reactions. Sloppy technique leads to some bleached fibers taking on a blue color, or some unbleached fibers taking on a red color.

Lofton-Merritt Stain. The Lofton-Merritt stain was developed to aid in distinguishing between unbleached sulfite and unbleached sulfate fibers. This stain is highly useful, once it has been checked against known fibers, but it is not reliable unless it is standardized every day. Lofton-Merritt stain is prepared as follows:

Solution A: 2 g. of Malachite green in 100 cc. of distilled water.
Solution B: 1 g. of basic fuchsine in 100 cc. of distilled water.

The two solutions are kept separately in tightly stoppered bottles and mixed together just before use. Ordinarily, the two solutions are mixed in the proportion of 1 volume of solution *A* to 2 volumes of solution *B*, but the ratio varies, depending upon the dyes used, and consequently the correct ratio must be determined on known samples of pulp. In making a batch of stain, it is best to mix the two solutions drop by drop until the correct color reactions are obtained with known fibers.

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[383] J. H. Graff, *Pulp and Paper Microscopy,* The Institute of Paper Chemistry, Appleton, Wisconsin (1942)

In using Lofton-Merritt stain, the compound stain is added to the fibers on the slide and allowed to remain two minutes. At the end of this period, the excess stain is removed by means of hard filter paper or, better, by playing a fine stream of distilled water at one end of the slide so that the water washes gently over the fibers. Then, three to four drops of 0.1% hydrochloric acid solution (1 cc. conc. HCl diluted to 1 liter of water) are added and left for about thirty seconds. The acid is then removed with a blotter and a few drops of distilled water added. A cover glass is then placed on top of the fibers and the slide pressed gently between two pieces of blotting paper to remove any excess water.

When properly made and used, Lofton-Merritt stain produces a blue to blue-green color with unbleached sulfate fibers and a purple or lavender color with unbleached sulfite fibers. Since a blue color is also produced with groundwood fibers, this stain can be used to determine the amount of unbleached sulfite in mixtures containing groundwood, unbleached sulfite, and unbleached sulfate fibers. Highly purified (i.e., bleached) fibers do not absorb any color. Some of the newer unbleached sulfate pulps do not stain well with this stain. In testing the stain, if any sulfite fibers are green, too much Malachite green is present. If any sulfate fibers are purple, too much fuchsine has been used.

Cooking (Bleachability) Stain. The cooking stain is useful as a means of measuring the approximate degree of cooking. In this staining technique, the fibers are first treated with a solution of Malachite green and then with a solution of Congo red. The colors produced range from green for relatively uncooked fibers to red for the completely cooked fibers. If green fibers predominate, the pulp is undercooked, whereas a predominance of red fibers indicates an overcooked pulp. Graff[384] gives the various colors the following arbitrary values:

Color	Extent of cooking
Variations of green	10%
Blue with green markings	20%
Red with strong green markings	40%
Red with faint tint of green	60%
Lightly broken red	80%
Pure red	100%

Graff and coworkers[385] found that the cooking stain correlates well with the lignin content and permanganate number for any given pulp.

Cyanine-Glycerine Reagent. Cyanine-glycerine reagent can be used to determine the bleachability of pulp. This reagent consists of a saturated alcoholic solution of cyanine diluted with water and one-third of its volume of glycerine. The following color reactions are obtained, according to Graff:[386]

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[384] J. H. Graff, *Pulp and Paper Microscopy*, The Institute of Paper Chemistry, Appleton, Wisconsin (1942)

[385] J. F. Hechtman and J. H. Graff, *Paper Trade J. 111*, No. 5: 52–56 (Aug. 1, 1940)

	Tracheids		Ray cells	
	Cell walls	Pits	Cell walls	Pits
Unbleached sulfites	Blue	Center deep blue, outside dark blue	Blue	Dark blue
Bleached sulfites	Colorless	Colorless	Colorless	Dark blue
Unbleached sulfates	Blue	Colorless	Blue	None present
Bleached sulfates	Colorless	Colorless	Colorless	Colorless

Bleach Stain. The bleach stain is useful for measuring the approximate degree of bleaching. This stain is based upon the amount of absorption of a basic dye, gentian violet, by the fibers. Lignin has a strong affinity for basic dyes and cellulose has little or no affinity, so that the amount of gentian violet absorbed by the fibers is related to the amount of lignin in the fibers. Thus, the color reaction is related to the bleach requirement of the pulp. Lightly bleached sulfite fibers stain a dark blue with this stain, whereas highly bleached sulfite fibers are stained only a faint color. Soda and sulfate fibers also stain in proportion to the degree of bleaching.

Shaffer Stain. The Shaffer stain,[387] which is made by dissolving 1 g. of C. P. brazilian in 175 cc. of water, has been suggested for distinguishing between bleached sulfite and bleached sulfate fibers. This stain is not used to any extent in fiber analysis.

Malachite Green Reagent. A 2% solution of Malachite green in acetic acid is useful in measuring the extent of bleaching, since unbleached fibers stain blue-green to green, partially bleached fibers stain blue, and fully bleached fibers show up colorless.

Groundwood Stains

It is often desirable to detect the presence or absence of groundwood fibers in papers without making a quantitative determination. This can be done by the use of special stains which are applied directly to the paper.

Phloroglucinol stain is made by dissolving 1 g. of phloroglucinol in 50 cc. of alcohol and 25 cc. of concentrated hydrochloric acid. It produces a carmine red color on papers containing groundwood. The depth of color is an indication of the amount of groundwood present. However, a very light color does not necessarily indicate the presence of groundwood pulp, since unbleached chemical wood fibers sometimes show a slight color with this stain. Jute generally produces a reddish color with this stain. The stain is relatively unstable and should not be made up long before being used.

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[386] J. H. Graff, *Pulp and Paper Microscopy,* The Institute of Paper Chemistry. Appleton, Wisconsin (1942)

[387] R. W. Shaffer, *Ind. Eng. Chem., Anal. Ed. 5,* No. 1: 35–36 (Jan., 1933)

Aniline sulfate stain produces a yellow color when applied to paper containing a high percentage of groundwood fibers. In addition, this stain also produces a yellow color with raw unbleached sulfite and sulfate pulps. To prepare aniline sulfate stain, 1 g. of aniline sulfate is dissolved in 50 cc. of distilled water and the solution acidfied with one drop of concentrated sulfuric acid.

Other groundwood stains include *p*-nitroaniline and dimethyl-*p*-phenylenediamine. The latter can be used to differentiate between bleached and unbleached pulps, since it produces an orange color with mechanical and unbleached sulfite pulps, and a yellow color with bleached sulfite pulp.

One interesting method for distinguishing between softwood and hardwood groundwood is to stain a slide first with aniline sulfate and then with aqueous methylene blue. When treated in this way, hardwood groundwood fibers generally stain a bluish green color, whereas softwood groundwood fibers stain yellow.

Stains for Special Fibers

Many special stains can be used for the detection and identification of special non-woody fibers. The stains which are used for this purpose are so varied that it is impossible to cover all of them, and the reader is referred to special reference books on the subject.[388] The physical properties of non-woody fibers are discussed in the chapter on pulp fibers.

A few of the stains which are useful for examining non-woody fibers are listed below:

Neocarmine can be applied to the fibers (after decolorizing and washing). The following are some of the color reactions obtained with different fibers, using a solution of Neocarmine W: linen, deep blue; cotton, reddish blue; jute, olive brown; wool, yellow; viscose, red; acetate rayon, light green-yellow.

With Neocarmine B, the following reactions are obtained: cotton, red; linen, blue.

Flax and hemp can be distinguished with cyanine. In making this stain, a saturated solution of cyanine in water is made and then this solution diluted with a small amount of water and about one-third of its volume of glycerine. The stained fibers on the slide should be heated and then washed with a solution containing glycerine, water, and alcohol. The slide can be mounted in glycerine. The colors obtained are: flax, colorless; hemp, greenish blue.

A determination of the amount of wool in paper is sometimes required for roofing paper and linoleum base stock. The amount of wool can be determined by any of the following methods: (*1*) solution in acid, (*2*) solution in alkali, (*3*) Kjeldahl method, (*4*) microscopic counting of fibers. The weight factor for wool fibers is 3.10 ± 0.28.[389]

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[388] J. H. Graff, *Pulp and Paper Microscopy,* The Institute of Paper Chemistry, Appleton, Wisconsin (1942)

[389] J. H. Graff, *Tappi 32,* No. 5: 212–213 (May, 1949)

Speck Analysis

It is frequently the job of the paper analyst to analyze and identify dirt specks in paper in order to determine the source of the dirt. In this work, the analyst must use his ingenuity, particularly in mills using waste paper or rags, since almost anything may be present in paper made from these materials. Many helpful hints are given in the literature, but it is sometimes necessary to devise new methods. In most cases, the dirt can best be examined under a dissecting microscope.

In analyzing dirt specks, the sample of pulp or paper is first wetted in water and then the marked specks are removed, using iridium needles and a dissecting microscope, or any microscope magnifying about 50 to 100 times. The specks can be arranged on a microscope slide and then identified either by chemical or solubility tests, or from the physical appearance of the specks. Browning and Graff have developed a chart for speck analysis which is used in certain paper mills. Most of the following methods have been taken from their chart. Some of the solubility tests used are as follows:

(*1*) Water—for dyestuffs and alum specks.
(*2*) Alcohol—for some dyestuffs.
(*3*) Alcohol plus 1% conc. HCl—for resins and pitch.
(*4*) Benzene—for resins, oil, grease.
(*5*) 5% Sodium hydroxide (at 100° C.)—for casein and wool.
(*6*) 10% Nitric acid—for copper and lead specks.
(*7*) Hydrofluoric acid—for silicate.

Some of the staining or treating agents used are as follows:

(*1*) Fiber stains—for identifying fibers.
(*2*) Phloroglucinol—for shives, bark, etc.
(*3*) Iodine-iodide solution—for starch spots.
(*4*) 2% Ferrocyanide solution—for copper (brown) and ferric iron (blue).
(*5*) India ink—for slime-forming bacteria.
(*6*) Millon reagent—for casein (brick red color).
(*7*) Raspail test (sugar and conc. H_2SO_4)—for rosin spots (raspberry red).
(*8*) Bleach solution—for shives, bark, etc. (which decolorize when treated with bleach solution).

Coal Specks. These are black, insoluble particles which are often in a pulverized condition, due to the action of the calender rolls. They can be distinguished from iron spots by testing with a magnetized needle, or by the ferrocyanide test. Large coal specks can be readily smeared when rubbed across the sheet. If the speck tends to break and show sharp edges, it is probably a cinder.

Iron Specks. Iron specks can be determined by treating the speck with 10% hydrochloric acid solution, removing the excess acid by draining onto a blotter, and moistening each speck with a small drop of potassium albumin fixative) and the paraffin removed by soaking with xylene. The slide can then be examined with transmitted light.

Special Staining Techniques

It is possible for an experienced observer to obtain considerable information on the type and location of sizing agents in paper by microscopic examination of the paper. This is particularly true with starch-sized papers where it is possible by staining with iodine-iodide solution to determine approximately how much starch is present, whether the starch was applied as a surface or internal size, and if sized internally, whether the starch is uniformly distributed throughout the sheet.

Special staining techniques can be used for detecting the presence of resins (pitch) in pulp fibers. Either Sudan orange 2R or Sudan black can be used for pitch detection. These dyes are dissolved in 72% alcohol-glycerine mixture (3 volumes of alcohol and 1 volume of glycerine) to form a saturated solution. Sudan orange stains pitch red, and Sudan black stains pitch blue. In using this method of staining, the dye solution is added to the fibers on the slide and left until the pitch spots are stained (approximately one hour for unbleached pulps and two to three minutes for bleached pulps), and then the excess dye is removed.

USE OF STATISTICS IN THE PAPER INDUSTRY

Theory of Statistics

In statistics, a universe is considered as being made up of a large group of related individual measurements which are known as the population. A normal universe is one in which the individual measurements are distributed in accordance with the Gaussian law of chance, known as the normal law.

The theory of statistics is based upon two fundamental concepts:[1] (*1*) that there must exist an equality of opportunity for the chance occurrence of each item and (*2*) that nature has a very precise and orderly plan for variation which is revealed whenever some variable factor is measured, and the items are grouped numerically in the order of increasing or decreasing magnitude. Thus, if a sufficient number of items are selected at random, these will appear in proportion to their frequencies, and the data thus secured may be used to construct a replica of the universe. This replica can then be studied by statistical methods. To be useful for this purpose, all data must be homogeneous, that is, all data must be obtained under the same test conditions.

In industrial applications, the primary concern is with estimating characteristics of the universe of data from the evidence in small samples. Statistics are of great value in handling the data obtained in sampling, instrumentation studies, paper testing, and quality control. Data may be of two types: (*1*) data representing single test measurements on a series of similar objects and (*2*) data representing a series of like tests on a single object. Most data are of the first type. The second type is used, however, to furnish information regarding errors of measurement.

Precision is the reproducibility or spread of results about the average. Accuracy is error or bias, and refers to the displacement of the mean result from the true average. Precision can be low, while accuracy of average is quite high. It is important in statistics to differentiate between accuracy and precision. Some of the purposes for which statistics may be used are: (*1*) to determine the accuracy of a given set of data; (*2*) to determine how many tests must be made to secure any specified precision; (*3*) to determine the variability of some property or group of properties; (*4*) to determine the factors which influence the variability of properties; (*5*) to determine when results are significant.

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[1] C. C. Forsaith, "Statistics for Foresters," Tech. Bull. No. 62, New York State College of Forestry, Syracuse, N. Y. (Mar., 1946)

The following is a general, illustrative approach to the application of statistics in the paper industry. It does not present an integrated attack on the problem of control in a paper mill, but instead illustrates some of the methods useful in analyzing paper testing data.

Methods of Comparison

There are two principal methods of testing or comparison. The first method, called the *method of attributes,* is typified by go-no-go gages, by which each item is tested to see whether it is within limits or outside limits. The other method, called the *method of variables,* is based upon an exact measurement for each dimension examined. The latter method requires greater skill in measuring, but it requires a smaller sample and makes possible more exact calculations. It is the method most widely used in the paper industry.

All things are variable if the method of comparison measures small enough differences. Variability is due to lack of precision of the measuring device or to inherent, non-uniformity of the quality being measured. Use of more precise measuring devices reduces the error, but there are limits to which this correction may be applied. A rough working rule is that the measurement scale should be several times as close and precise as the variation which it is desired to measure.[2] Repetition of the test reduces the error, since the error of average is inversely proportional to the square root of the number of observations. This law, which is known as the law of least squares, states that (*1*) the precision of the results obtained is proportional to the square root of the number of readings made; (*2*) the degree to which a sample is representative of the whole is proportional to the square root of the number of specimens taken; (*3*) the degree to which the effect of a given condition (when all other conditions are constant) is reflected in the results is proportional to the square root of the number of runs made.

Rules of Sampling

Any universe can be specified in detail by a number of mathematical constants, or statistics. If the statistics of the universe are known, it is very easy to calculate the statistics of samples taken from the universe. In practice, however, the process is reversed, in that samples are taken and analyzed, and from these data the statistics of the universe are then calculated with a degree of precision which depends upon the number of values making up the sample. Sampling is used when the whole data are too large to be handled by themselves. In this way, generalizations can be made about the entire population from an analysis of the sample. The accuracy of sampling should be governed by the precision of the analytical methods, since it is illogical to apply analytical methods of high precision to a sample which may have a large error. Conversely, it is wasteful to spend the time taking highly accurate samples for testing by analytical procedures of low precision.

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[2] J. H. Toulouse, *Tappi 33,* No. 1: 44–48 (Jan., 1950)

There are general rules for the sampling of fluids from a batch, solids from a batch, fluids in flow, and solids in movement. These rules are described in books on engineering principles. The taking of samples must be completely random, so that the selection is purely by chance and each item has an equal opportunity of being selected. The sample must have the same degree of variation and the same distribution of the different degrees of variation as the original material from which it was taken; in other words, it must be a representative sample. A perfect sample should represent a precise model of the population.

All samples must, of course, be protected from change after sampling and before testing. In commercial work, sampling methods must be carefully agreed upon by both the consumer and producer, since many different sampling plans may be used. Testing methods and calibration of testing instruments must also be carefully specified in advance. For most purposes, TAPPI or A.S.T.M. standard methods of sampling, testing, and calibration can be used in writing specifications.

In order to set up an adequate control system, data for design of its final form must be taken at a time when there is no variation in the system, other than chance sampling. In other words, control must come first so that the samples will be taken under the same conditions at all times, with no disturbing environmental influences. There must be no unknown or unrecognized causes of variability in the quality of the product or, in the words of Shewhart,[3] there must be no assignable causes of variability. Assignable causes of variation are due to differences in machines and in sources of raw materials. Chance causes are due to peculiarities of the machine, skill of the operators, etc., which may be considered as normal.

Samples are rarely a true replica of the universe, so that the question arises as to how large a sample should be taken to obtain the desired precision. This can be answered from a study of the frequency distribution curve, which shows the variations to be expected in the material to be tested. The method of constructing a frequency distribution curve will be taken up shortly. If the frequency distribution is normal, certain exact mathematical calculations can be applied to the measurement to be made on the material. For example, the range within which 99.7% of the fraction defective of values obtained by a series of samplings would be expected to fall can be expressed by

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[3] W. A. Shewhart, *Economic Control of Quality of Manufactured Product,* D. Van Nostrand Co., New York, N. Y. (1931)

$$\bar{P} \pm 3\sqrt{\bar{P}(1-\bar{P})/n}$$

where $\bar{P}$ equals the average fraction defective of values from a number of groups and n equals the number of samples used in each group. This equation shows that it is necessary to quadruple the sample size in order to double the precision.

The practical or specific probability curve for the material in question may not be exactly the same as the normal probability curve, but it is assumed in statistical analysis that the set of figures is drawn from normal distribution. It is true, moreover, that the distribution of the means of small subgroups of values gives a curve very close to normal, even when the original frequency curve is considerably different from normal.

Grouping and Analyzing Data

Statistical methods for handling data consist of (*1*) grouping the data into easily understood form and (*2*) analyzing the data by accepted methods. Most original data are obtained in chronological order and consequently may need to be regrouped to be easily understood. One method is to arrange the data according to ascending order of magnitude in a series called an ungrouped frequency distribution. This simplifies the analysis, but is unsuitable for the handling of large amounts of data. Data may be presented in a grouped frequency distribution by dividing the data into a number of conveniently sized groups, called class intervals or cells, which are arranged in a column of decreasing size. A frequency distribution can then be constructed from these grouped data by checking each value according to the class interval into which it falls. This gives the number of times a measurement falls in that class interval.

Frequency Distribution Curve

A grouped frequency distribution curve can be obtained by plotting the data from the grouped frequency distribution, using the interval groupings as the X-axis and the frequency as the Y-axis. In other words, the frequency distribution curve is obtained from the data as follows:

(*1*) The range of the largest and smallest value is determined. These values are then plotted on the X-axis.

(*2*) The above range is then divided into equal class intervals. There are definite rules for the choice of number of intervals. In general, there should be about 12 to 20 class intervals, about 7 or 8 for each 100 measurements. The boundaries of the cells should be halfway between two possible observations.

(*3*) The class frequencies are then determined as the number of items in each class interval.

(*4*) Finally, the class frequencies (ordinates) are plotted against class intervals (abscissae).

If desired, relative frequency can be plotted in place of frequency. The relative frequency is a percentage which is obtained by dividing the frequency of each class interval by the total number of observations. Thus, the relative frequency is the fraction of the total number of observations lying within each class interval.

If a symmetrical bell-shaped curve, which meets the other qualifications of a normal probability curve, is obtained by the above procedure, it is taken as an indication that the values vary according to the laws of normal probability, and that the sample is a good replica of the population from which it was taken. The goodness of fit of the sample curve with a normal bell-shaped curve will show whether there is anything abnormal about the sample. A normal probability curve is represented in Figure XVII-1.

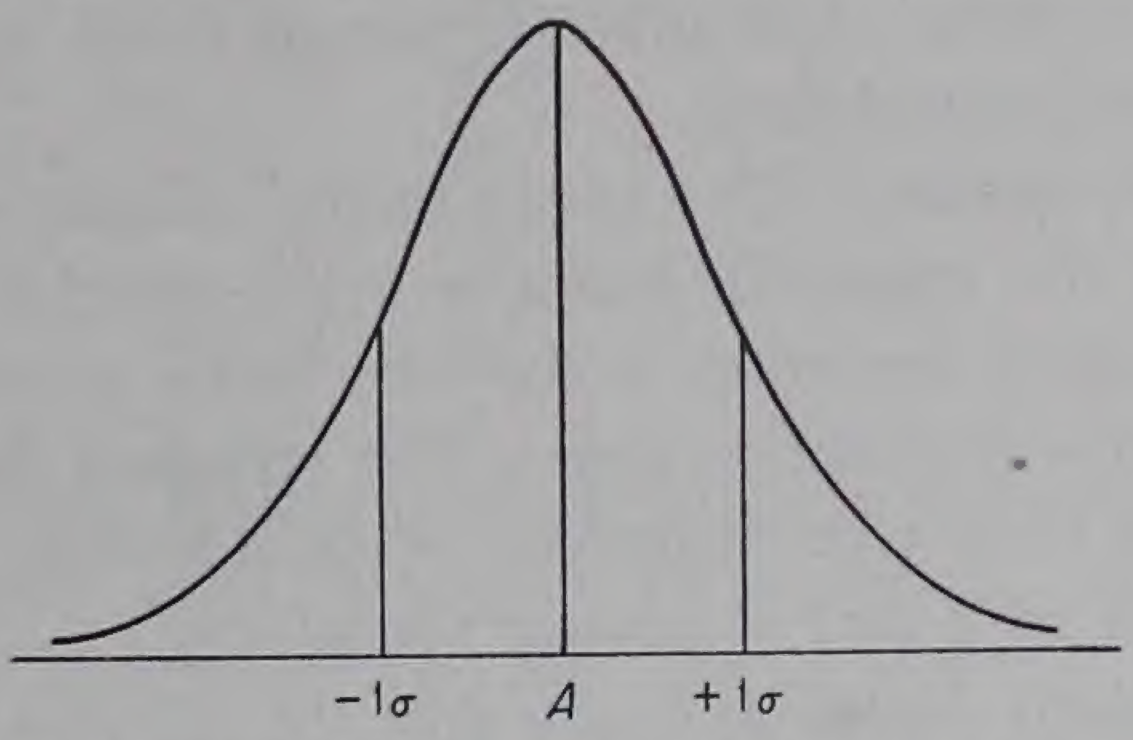

Fig. XVII-1. Normal probability curve.

This curve is symmetrical to A, which is the average or mean value of the quantity being measured. Other characteristics denoted by this curve are that small deviations from the average are more frequent than large deviations and that positive deviations occur as often as negative deviations.

Characteristics of Frequency Distribution

Grouped frequency distribution curves greatly condense the original data, but it is frequently desirable to use characteristics or statistics of the frequency distribution to condense the data further. Two properties of the data are most important, the average (mean) and the variability. The variability can be expressed in a number of ways, the most important of which are range, standard deviation, and variance. Other characteristics of frequency distribution are sometimes used, but most of these are falling into disuse because of certain shortcomings or because of their lack of suitability for industrial work. The number of observations should always be given.

Average or Mean. The average of the test values may be calculated as the arithmetic mean ($\overline{X}$), that is, the sum of the variables divided by the number of units. In statistics, a bar over the symbol indicates an average of that value. The mean is the most widely used statistic, but it is badly distorted by extreme values and fails to give full information about a sample. Because of the large influence of extreme values, it is customary in calculating the mean to discard extreme values, but particular care should be exercised in carrying out this procedure if the number of observations is small.

The mean of a small group of individual items may be obtained by adding all items and dividing by the number of items. However, when a large number of items is to be analyzed, this method is too cumbersome, and it is then necessary to obtain the mean from grouped data. This is done on the assumption that all values in a class interval are distributed evenly.

Range. Range is the difference between the largest and the smallest values. Range furnishes limited information, since it gives nothing about the intermediate results. The greatest use of range is in quality control charts, as will be explained later.

Standard Deviation. The most useful measure of variability of the test values is the standard deviation represented by the Greek letter sigma (σ). Standard deviation is the root mean square deviation of the test values from the arithmetic mean. The standard deviation is of value for comparing the scatter or dispersion of sample data with that obtained in other studies, or with that of normal probability.

A small standard deviation means that the values are closely clustered about the arithmetic mean, whereas a large standard deviation means that the values are widely scattered. In Figure XVII-1, σ is the point of inflection of the curve and represents one standard deviation. The area under the curve between the two ordinates $-\sigma$ and $+\sigma$ represents the relative likelihood or the probability of occurrence of a value in the range between these ordinates. In the normal distribution curve, the percentage of the total numbers included in the limits for 1, 2, and 3 standard deviations are as follows:

$$\overline{X} \pm 1\sigma\text{—}68.3\%$$

$$\overline{X} \pm 2\sigma\text{—}95.5\%$$

$$\overline{X} \pm 3\sigma\text{—}99.7\%$$

50% of the area of the curve falls within the limits of $\pm$ 0.67 σ, which means that any value chosen at random has a fifty-fifty chance of falling within this range. Table I gives the total percentages of items included for different ranges of σ above and below the mean. Thus, if a given distribution has an average of 100 and a standard deviation of 5, the chances are 1 to 21 that any given figures will fall outside the range of 90 to 110 (because this range is plus or minus 2 deviations). On the other hand, if the distribution has an average of 100 and a standard deviation of 1, then the chances are 1 to 15,772 that any given figure will fall outside the range of 96 to 104.

TABLE I

Table of Probability Integrals

Number of standard deviations (σ) above and below the mean	Percentage of total items included in specified range	Chance of any item, taken at random, falling within given range
0.2	15.9	0.2 : 1
0.4	31.1	0.5 : 1
0.6	45.1	0.8 : 1
0.8	57.6	1.4 : 1
1.0	68.3	2.2 : 1
1.2	77.0	3.3 : 1
1.4	83.8	5.1 : 1
1.6	89.0	8.1 : 1
1.8	92.8	12.9 : 1
2.0	95.5	21.0 : 1
2.5	98.8	79.6 : 1
3.0	99.7	369.4 : 1
3.5	99.8	2126.6 : 1
4.0	99.9	15771.8 : 1
4.5	99.9	147057.8 : 1

In ungrouped data, the standard deviation is obtained by *(1)* obtaining the difference between each value and the arithmetic mean, *(2)* squaring each difference and then averaging the square, and *(3)* taking the square root of the total. The definition of standard deviation is:

$$\sigma^2 = \frac{\Sigma(X - \overline{X})^2}{n},$$

but a more convenient formula is:

$$\sigma^2 = \left[\Sigma(X^2) - \frac{(\Sigma X)^2}{n}\right]/n$$

A problem taken from Forsaith[4] serves to illustrate the calculation of standard deviation from ungrouped data.

Five fibers from the wood of *Pinus lambertiana* Dougl. were measured, and the following lengths were obtained: 4.35, 7.35, 4.65, 6.45, and 4.35 mm. The sum of these lengths (27.15 mm.) divided by 5 gives the average $\overline{X} = 5.43$ mm. The deviations from the mean will be:

$$\begin{array}{cccc}
X & \overline{X} & X_1 & X_1^2 \\
4.35 & -\ 5.43 = & -1.08 & 1.166 \\
7.35 & -\ 5.43 = & 1.92 & 3.686 \\
4.65 & -\ 5.43 = & -0.78 & 0.608 \\
6.45 & -\ 5.43 = & 1.02 & 1.040 \\
4.35 & -\ 5.43 = & -1.08 & 1.166 \\
\hline
 & & & 7.666
\end{array}$$

The standard deviation is $\sigma = \sqrt{7.666/5} = 1.24$ mm.

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[4] C. C. Forsaith, "Statistics for Foresters," Tech. Bull. No. 62, New York State College of Forestry, Syracuse, N. Y. (Mar., 1946)

The standard deviation (1.24 mm.) thus obtained proved to be less than that (1.40 mm.) obtained from the analysis of a far larger number of fibers. This may be due to a failure to pick items towards the limits of the range, a probability which may be counteracted by using $n-1$ in place of n in the above formula. When this is done, the standard deviation is found to be 1.39 mm., which is very near to the value obtained by using a far greater number of items. The number $(n-1)$ is known as the degrees of freedom of the deviation, which is defined as the number of observations minus the number of constraints on the system.

It may be safe to employ the following general rules with respect to the use of a small number of items: (*1*) if the range of the small sample in comparison with that of the population is cramped (less than 50%), use $n-1$; (*2*) if the range of the small sample is 50% or more of that for the entire population, use n; (*3*) if the ranges are nearly equal to that of the parent, use $n+1$; (*4*) if the total number of observations is less than 25, use $n-1$.

Values	Differences from arbitrary mean of 50	Square of differences
49	−1	1
50	0	0
51	+1	1
53	+3	9
52	+2	4
50	0	0
48	−2	4
52	+2	4
49	−1	1
50	0	0
Sum of differences	+4	*24*

Adjustment for mean $= 50 + [+4/24] = 50.17$
Correction factor $= (4)^2/10 = 0.8$
Corrected sum of squares $= 24 - 0.8 = 23.2$
Mean square of deviations $= 23.2/n-1 = 23.2/9 = 2.58$
Estimated standard deviations $= \sqrt{2.58} = 1.61$

In grouped data, the standard deviation is obtained by (*1*) getting the average deviation of each group from the arithmetic mean, (*2*) squaring this average deviation for each group, (*3*) multiplying by the frequency for each group, (*4*) adding the totals and dividing by the number of items, and (*5*) taking the square root of the sum.

In order to lighten the arithmetic calculations, it is often desirable to shift all values to a new scale. For example, in the above example, it would be convenient to subtract 4.35 from all values of X, thus giving as the fiber dimensions 0, 3, 0.3, 2.1, and 0 which are easier numbers to handle. This shifting does not alter the variance, since the variability is not affected by changes in the mean. This procedure is most beneficial when using the alternative formula for calculating σ.

Another way of avoiding work with decimals is to use an arbitrary mean of a whole number. Deviations are then taken from this whole number and a correction factor applied at the end, as shown on p. 988, where 50 is taken as an arbitrary mean in place of the true mean of 50.4.

Variance. The magnitude of the variability can be determined from a property of the data known as the variance. The variance of a set of numbers is taken as the sum of the squares of the deviations from the mean divided by the number. In other words, the variance is the mean square. It is equal to the square of the standard deviation. When small samples are used, the divisor is taken as the number of independent values from which the sum of the squares is composed, i.e., usually one less than the number of quantities.

Coefficient of Variation. The coefficient of variation (V) is a measure of the relative dispersion. It serves to compare two instances in which the same absolute dispersion occurs about two unequal arithmetic means. It is a percentage obtained by dividing the standard deviation by the arithmetic mean, as follows: Coefficient of variation $(V) = (\sigma/\overline{X}) \times 100$. It is the standard deviation calculated on a mean of 100.

Limits of Reliability

In many cases of technical analysis, a single sample is taken as representative of the aggregate. It is often desirable to know the adequacy of the sample in representing the whole. The limits of reliability can be expressed in terms of the probable error, maximum error, or the standard error. For example, the results may be expressed as $\overline{X} \pm$ probable error. In many cases, it is useful to use the formula $\overline{X} \pm a\sigma$, in which a is obtained from tables based upon the number of observations made and the statistical probability.[5]

Standard Error. A very useful statistic in the handling of sample data is the standard error (SE_m) of the mean, or in other words, the difference between the mean obtained from the analysis of chance samples and the true mean of the universe. The value of the standard error depends upon (*1*) the degree of variability of the items in the universe from which the sample was taken, as measured by the standard deviation, and (*2*) the number of items taken for the determination of the standard deviation of the universe. The formula for SE_m, the standard error of the mean, is $SE_m = \sigma/\sqrt{n}$.

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[5] *A.S.T.M. Manual on Presentation of Data,* p. 41. Published by the American Society for Testing Materials, Philadelphia, Pennsylvania (1940)

As stated above, SE_m theoretically represents the standard deviation of the individual means of different samples about the perfect mean of the universe, σ the theoretical standard deviation of the items in the universe, and n the number of samples tested.[6] In practice, however, it is customary to let SE_m equal the standard error of a single computation, σ the standard deviation of the items included in the sample about the mean of the sample, and n the number of items in the test. This distortion of the true values can be justified on an empirical basis. It has been found from experience that when 30 or more readings are taken, the probability is two to one that a mean obtained by a single analysis will not deviate from the perfect mean by more than one standard error, 21 to 1 by more than two standard errors, and over 300 to 1 by more than three standard errors[6] (see Table I). Stated differently, it means that the true value would fall within ± 1 standard error from the arithmetical mean in 68 times out of 100, within ± 2 standard errors 95.5 times out of 100, and within ± 3 standard errors 99.7 out of 100. For example, in a problem where $SE_m = 0.076$ and $\overline{X} = 3.441$, the chances are 2 to 1 that the true mean lies somewhere between the limits of $\overline{X} \pm SE_m$ or 3.441 ± 0.076, and 19 to 1 between the limits of $\overline{X} \pm 2SE_m$ or 3.441 ± 0.152. As another illustration, suppose that an analysis of 81 samples of paper shows that the average basis weight is 60 lb. and the standard deviation is 1.89. The standard error is then $SE_m = 1.89/\sqrt{81} = 0.21$, which means that the average of a second set of samples would have a two to one chance of falling within the range of ± 0.21 lb. from the average of the first set, or within the range of 59.79 to 60.21.

Probable Error. The probable error is 0.6745 of the standard deviation. It is the error which will not be exceeded by 50% of the cases, or in other words, it is the error on either side of which any deviation from the true average is equally likely to fall. $\text{P.E.} = 0.6745\ \sigma/\sqrt{n}$. The use of the probable error is decreasing because of its lack of meaning.

Maximum Error. The maximum error is considered to be 3σ, which normally includes 99.73% of all values measured. In other words, the maximum error is not the greatest possible error, but rather the error which will not be exceeded in over 0.27% of all cases.

Significant Figures. In obtaining data, the apparent degree of precision should not be carried in excess of that justified by the data. To carry a value beyond the significant figures involves unnecessary work and implies a relative precision which is not justified. As a general rule, computations should not be carried more than two places beyond the least reliable measurement included in the data, that is, if the observed values are read to the nearest 0.1 lb., the figures should be carried to the nearest

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[6] C. C. Forsaith, "Statistics for Foresters," Tech. Bull. No. 62, New York State College of Forestry, Syracuse, N. Y. (Mar., 1946)

0.001 lb.[7] Rejection of figures should be done after computations, according to the general rules for rounding off figures.

The problem often arises as to what data in a compilation of data should be discarded. Extreme values obtained in large sets of data can be discarded so that all extreme values which are recorded have significance in terms of their probability of occurrence.[8] However, any values outside 3 standard deviations indicate assignable causes of variation and may be disregarded in computation only if the causes are identified and steps taken to prevent their recurrence.

Tests of Significance

It is often of importance to know (*1*) whether or not a given individual or a given sample of n individuals belongs to a certain population or (*2*) whether or not there is any significance between the means of two different sets of numbers, i.e., whether the two sets can be considered as being drawn from the same or from different populations. These are known as tests of significance.

Tests of significance are based upon the probability of occurrence. Probability is generally expressed on a scale of 0–1, or on a percentage basis. Zero probability means that a certain event will not occur, whereas a probability of 1 means that the event is certain to occur. A probability of 0.05 means that there is a 5% probability of occurrence. A probability level of 95% is generally used in industrial work as a test of significance, which means that the event will occur 19 out of 20 times. It means that 95% of the individuals lie between $-1.96\,\sigma$ and $+1.96\,\sigma$ of the mean. Larger values of probability are an even stronger indication that the results are significant.

The data can be used in one of two ways. They can be used (*1*) to determine the number of items to be measured for a specified precision or (*2*) to determine the significance of differences between means. Both types of problems are illustrated below.

Determining the Number of Items to Be Measured for a Specified Precision. The problem often comes up of how many tests must be made to obtain an average which will not differ by more than some quantity from the true average in a certain percentage of cases. Variance must be taken into account, since a small variance means that a fewer number of tests will be required to determine a value with a given precision than is the case when the variance is large. Problems of this sort are handled on the basis that sample means distribute themselves about the population mean with a standard deviation equal to $\sigma/\sqrt{n}$, or 1 standard error. Thus, if the mean of n samples taken from the population is more than $1.96\,\sigma/\sqrt{n}$ (95% probability) different from the true mean, it can be concluded that the sample was not drawn from the population under consideration.

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[7] *A.S.T.M. Manual on Presentation of Data,* pp. 44–45. Published by the American Society for Testing Materials, Philadelphia, Pennsylvania (1940)

[8] C. C. Forsaith, "Statistics for Foresters," Tech. Bull. No. 62, New York State College of Forestry, Syracuse, N. Y. (Mar., 1946)

In tackling a problem of the above type, the range allowed must first be stated as an absolute or relative value. A series of tests is made to determine the mean and the standard deviation. Then, using the formula for the standard error of the mean, $SE_m = \sigma/\sqrt{n}$, the necessary number of tests can be calculated. A problem from Forsaith[9] serves to illustrate. In this problem, the question is asked: How many fibers should be measured in order to obtain a mean which shall not deviate from the true mean of the population by more than 5% of the average length, and with a 95% probability which, as stated above, is the accepted probability level for problems of this sort. First, the mean and standard deviation for a single analysis are obtained, and then these are used to determine the number of items which should be chosen for a subsequent sample in order to insure the above accuracy. Assume that the data have shown a mean of 3.44 and a standard deviation of 0.630. Then, 5% of the calculated mean is $3.44 \times 0.05 = 0.172$ mm. A 95% probability is 19 to 1, or approximately 2 standard errors. The number of samples to be tested (n) can be calculated as follows, where E equals the expected value of the mean and $\overline{X}$ equals the mean of the sample.

$$(1) \qquad t = \frac{\overline{X} - E}{SE_m} \qquad \text{or} \qquad \overline{X} - E = tSE_m$$

$$(2) \qquad t = \frac{d}{\sigma/\sqrt{n}} \qquad\qquad d = \frac{t\sigma}{\sqrt{n}}$$

$$(3) \qquad n = \left(\frac{t\sigma}{d}\right)^2 = \left(\frac{2 \times 0.63}{0.172}\right)^2 = 54 \text{ fibers}$$

The same technique can be used to evaluate the number required for any deviation or any probability, provided the constants are made available by a previous analysis consisting of at least 30 items.

Comparison of Means. In comparing results obtained on two or more materials from different sources, the problem often arises of determining the significance of means. A typical example is the comparison of bursting strength readings obtained on two different lots of paper. If the means of the two samples are fairly close together, there will be considerable overlapping of individual readings. The problem may be (*1*) to determine whether there is a significant difference in means or (*2*) to determine how many readings must be taken to reduce the chance of selection to a given probability. A single reading on each paper will tell practically nothing about the comparative status of the two papers, but by increasing the number of readings in each set, the means will vary within narrower limits, i.e., the probability curve will show less spread.

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[9] C. C. Forsaith, "Statistics for Foresters," Tech. Bull. No. 62, New York State College of Forestry, Syracuse, N. Y. (Mar., 1946)

In practice, the number of readings in each set is increased until the chances of mistake reach the point of acceptable risk. The standard deviation of the individual readings should first be obtained either from previous knowledge of the usual spread, or by direct calculation from 30 or more readings. A working rule used by some[10] is to increase the number of readings until the standard deviation of the two sets is reduced to 0.4 times the difference it is desired to distinguish with reasonable certainty. The general equation used for more exact calculations[11] is as follows:

$$t = \frac{\overline{X} - \overline{X'}}{\sigma}\sqrt{\frac{n_1 \times n_2}{n_1 + n_2}}$$

where $\overline{X} = \Sigma(X)/n_1$, $\overline{X'} = \Sigma(X')/n_2$, and

$$\sigma^2 = \frac{\Sigma(X'^2) - \frac{[\Sigma(X')]^2}{n_2} + \Sigma(X^2) - \frac{[\Sigma(X)]^2}{n_1}}{n_1 + n_2 - 2}$$

The value of t obtained by substitution of values in the above equation is compared with the required value of t for the probability level and degrees of freedom $(N_1 + N_2 - 2)$ obtained from suitable tables (see Table II[11]).

Toulouse[12] has reported on an extensive study made on two different kraft liner papers having the following characteristics:

	Board *A*	Board *B*
Number of tests	100	100
Maximum burst	117 p.s.i.	124 p.s.i.
Minimum burst	74 p.s.i.	89 p.s.i.

When grouped in subgroups of three, board *A* had an average of 95.68 and board *B* an average of 105.69. Calculations show that grouping in this way made it possible to distinguish the stronger from the weaker only 90% of the time, and that grouping in subgroups of 12 was required to distinguish between the two papers every time. From this, it can be concluded that when two normal kraft boards are only 10 p.s.i. apart in bursting strength, samples of twelve are required to conclude with certainty that the series of tests are different. In order to differentiate with the same certainty in the case of two boards differing by 5 p.s.i., a grouping of twenty-four values

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[10] P. H. Prior, *World's Paper Trade Rev. 111:* TS 50–58, 66–70, 91–96 (Apr. 7, May 5, June 2, 1939)

[11] K. A. Brownlee, *Industrial Experimentation,* Chemical Publishing Company, Brooklyn, N. Y. (1947)

[12] J. H. Toulouse, *Tappi 33,* No. 1: 44–48 (Jan., 1950)

TABLE II

VALUES OF t

Degrees of freedom	t				
	0.10	0.05	0.02	0.01	0.001
1	6.31	12.71	31.82	63.66	636.62
2	2.92	4.30	6.97	9.93	31.60
3	2.35	3.18	4.54	5.84	12.94
4	2.13	2.78	3.75	4.60	8.61
5	2.02	2.57	3.37	4.03	6.86
6	1.94	2.45	3.14	3.71	5.96
7	1.90	2.37	3.00	3.50	5.41
8	1.86	2.31	2.90	3.36	5.04
9	1.83	2.26	2.82	3.25	4.78
10	1.81	2.23	2.76	3.17	4.59
11	1.80	2.20	2.72	3.11	4.44
12	1.78	2.18	2.68	3.06	4.32
13	1.77	2.16	2.65	3.01	4.22
14	1.76	2.15	2.62	2.98	4.14
15	1.75	2.13	2.60	2.95	4.07
16	1.75	2.12	2.58	2.92	4.02
17	1.74	2.11	2.57	2.90	3.97
18	1.73	2.10	2.55	2.88	3.92
19	1.73	2.09	2.54	2.86	3.88
20	1.73	2.09	2.53	2.85	3.85
21	1.72	2.08	2.52	2.83	3.82
22	1.72	2.07	2.51	2.82	3.79
23	1.71	2.07	2.50	2.81	3.77
24	1.71	2.06	2.49	2.80	3.75
25	1.71	2.06	2.48	2.79	3.73
26	1.71	2.06	2.48	2.78	3.71
27	1.70	2.05	2.47	2.77	3.69
28	1.70	2.05	2.47	2.76	3.67
29	1.70	2.04	2.46	2.76	3.66
30	1.70	2.04	2.46	2.75	3.65
40	1.68	2.02	2.42	2.70	3.55
60	1.67	2.00	2.39	2.66	3.46
120	1.66	1.98	2.36	2.62	3.37
∞	1.65	1.96	2.33	2.58	3.29

would have to be used. To obtain the same certainty with boards differing by 3 p.s.i., a grouping of 48 would be required.

As a further example of the usefulness of the methods outlined, consider the problem[13] of a mill which is purchasing wood from a number of suppliers. It is known that these suppliers are obtaining wood from different areas, and consequently it appears probable that the wood will vary in response to the different conditions under which it is grown. For the purpose of the mill, the wood which has the greater density is preferable, since it will produce more pulp per cord, and the price per cord from all suppliers is probably the same. In a case like this, it is essential that the wood from all suppliers be sampled and tested under conditions which will give a high degree of precision in the resulting averages, since thousands of dollars' worth of wood may be purchased on the basis of the tests. On the other hand, the wood may be known to be of low density and, as a result, be purchased at a reduced price in comparison with wood of higher density. The question in this case is whether or not the price concession is sufficient to justify purchase of the low density wood. Here again, the precision of the sampling and testing procedure must be of a high order. An example based on the actual experience of one mill in sampling purchased pulp wood is given in Table III. The figures tabulated were obtained as a result of sampling large shipments of spruce wood from two sources. Because the size of samples is large in this case, n can be used in place of $n-1$. The formula then becomes

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[13] Problem taken from pamphlet, "Sampling Theory and Practice," New York State College of Forestry, Syracuse, N. Y.

$$t = \frac{\overline{X} - \overline{X}'}{\sigma_D}$$

where

$$\sigma_D^2 = \sigma_1^2/n_1 + \sigma_2^2/n_2.$$

It will be seen that the difference between the densities of the woods from these two sources is 1.93 lb. per cubic foot, and this difference is several times as large as the standard error of the averages themselves. Calculation of t using the above formula shows that the difference noted is truly significant. Therefore, purchase of wood from source II should result in a marked decrease in wood cost per ton of pulp, assuming that the cubic content of solid wood per cord from both sources is the same.

Comparison of Variances

In the above sections, it has been shown how to compare the mean of two groups of numbers. Another problem frequently encountered in industrial work is the comparison of the variabilities of two groups of numbers.

In laboratory experiments, it is possible to hold all variables constant while the variable under observation is changed, but this classical laboratory method is almost impossible to apply in industrial work. Statistical methods of analysis can be applied in mill experimentation, however, whereby the particular variables to be studied are selected, and each of these variables changed separately. The assumption is made that the effects of other variables are at random and that they will show in the measure-

TABLE III

Variation of Density of Pulpwood from Two Sources

Oven-dry density on green volume lb./cu. ft.		Wood from source I,	Wood from source II,
Class intervals	Class midpoint	frequencies	frequencies
16.0 to 16.99	16.5	1	
17.0 17.99	17.5		
18.0 18.99	18.5		
19.0 19.99	19.5	3	3
20.0 20.99	20.5	3	1
21.0 21.99	21.5	15	2
22.0 22.99	22.5	31	4
23.0 23.99	23.5	62	6
24.0 24.99	24.5	74	7
25.0 25.99	25.5	80	4
26.0 26.99	26.5	107	12
27.0 27.99	27.5	115	27
28.0 28.99	28.5	82	27
29.0 29.99	29.5	73	25
30.0 30.99	30.5	53	27
31.0 31.99	31.5	31	20
32.0 32.99	32.5	13	10
33.0 33.99	33.5	10	7
34.0 34.99	34.5	3	4
35.0 35.99	35.5	3	3
36.0 36.99	36.5	1	2
37.0 37.99	37.5		1
		760	192

Analysis of the data given above produces the following results

Spruce wood from source I		
Mean density	27.04	lb./cu. ft.
Standard deviation	2.85	" " "
Standard error of mean	0.103	" " "
Spruce wood from source II		
Mean density	28.97	" " "
Standard deviation	2.58	" " "
Standard error of mean	0.186	" " "

ments as variance due to experimental (residual) error.[14] In a study of this sort, all test results will tend to group themselves about the true average in an orderly way, except where there have been assignable causes of variation due to changes in one of the variables. Thus, it is possible to measure the size of the variance for each property measured, compare with the residual variance, and then compute the probability of its occurrence. By conducting an experiment in this way, information is obtained on how the effects of one variable are affected by the other variables, i.e., the effect of interaction. The mathematical calculations involved have been well described in other sources.[15]

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[14] H. G. Burbidge, *Pulp Paper Mag. Canada 51,* No. 3: 168–173, Convention Issue (1950)

Use of Statistics in Quality Control

Definition of Quality. The word "quality" is used in many different ways, and consequently it is necessary to define the term before it is used. In general, quality refers to the goodness of the product, so that a high quality product is considered as a good or excellent product. Quality has both an objective and a subjective side.

The most useful index of quality is a sum of those characteristics which are of importance to the user of the product. No properties which are not of significance to the customer should be included in the quality index. Each significant characteristic should be weighted according to its demerits or seriousness.[16]

Before paper quality can be measured, some means must be found for expressing quality in terms of the physical characteristics of the paper. The significant characteristics of paper quality may include variables such as weight, tensile strength, and moisture, or attributes such as wrinkling and dirt counts.[17] Such rigid specifications as complete freedom from wrinkles, holes, and dirt specks should not be included because they are obviously not capable of being met in large shipments of paper. A good specification can be obtained only after a thorough study of the consumer's needs and the manufacturer's product and processes, which means that a minimum of six months to one year is usually required to obtain the necessary information.[18]

Value of Quality Control. The value of quality control is undisputed. All industrial products are variable in quality, and it is therefore desirable to state the probability with which a given sample will fall within specific limits. Quality control provides a statistical means of detecting lack of control of quality. Once quality control is established, there will be a saving in cost, due to fewer rejects and less need for inspection.

Normal Quality Level. Once a means of measuring quality has been found, a normal quality level must be established to have a yardstick by which assignable causes of variation can be detected.[19] This means setting up limits of variability outside of which it is worth looking for assignable causes of variation. After the limits within which the data should fall have been established, any values falling outside these limits are an indication of the existence of causes of variability which can be found and eliminated.[20]

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[15] K. A. Brownlee, *Industrial Experimentation,* Chemical Publishing Company, Brooklyn, N. Y. (1947)

[16] J. B. Catlin and J. G. Strieby, *Paper Trade J. 125,* No. 15: 161–164 (Apr. 10, 1947)

[17] J. G. Strieby, *Paper Trade J. 124,* No. 24: 515–521 (Dec. 9, 1948)

[18] *Idem.*

[19] *Idem.*

Statistical methods have been of great value in quality control and are now being used in the paper industry.[21, 22] In practice, quality control resolves into the problem of determining from a given set of data representing fluctuations in quality of the product whether or not the product is under control. Prior to setting up control charts, it is necessary to obtain basic data from which chance variability may be calculated for the particular process. These data must be based on results obtained over a long enough period to determine whether the process is truly uniform. Then, statistics can be used for setting up limits within which future results must fall.

The specification of quality should include some statistic of the product. This may be simply the number of defective individuals or the percentage of defective individuals;[23] or the statistic may be more complex, such as the average (arithmetic mean) of the test values or a measure of the variability, such as a multiple of the standard deviation or the range. The number of demerits per unit may be plotted against the time at which samples were taken. Another more satisfactory method, which eliminates the varying width of control area due to size of samples, consists of plotting the standard deviation of demerits per unit against the time at which samples were taken.

Construction of Frequency Distribution. All statistical methods are based upon the fact that the data, when obtained under constant controlled conditions, can be plotted so that they result in a symmetrical curve known as the normal distribution, or probability, curve (see Fig. XVII-1). Changes in the probability curve can occur because of changes (either scheduled or unscheduled) in the processing conditions. It is of prime importance to know whether changes in the curve are due to a change in average value (i.e., a shift of the curve to the right or left), or due to a lack of uniformity (i.e., a change in the shape of the curve), since the remedy is different in each case. When the process is operating satisfactorily, the average will be centered between the specification, and the curve will be narrow and symmetrical with a predetermined relationship between its heighth and its width.

Since the practical use of statistics prevents the testing of all the product, it is customary to take samples at random. This still gives a large group of data which is hard to analyze, but which can be handled by statistical methods. Even though the original test measurements are not normal, it has been found that a very nearly normal distribution can be obtained by averaging small successive subgroups of the data and making a frequency distribution of the averages.[24] The subgroups should be selected so that variations within subgroups may be considered as due to chance causes, even though variations between subgroups are due to assignable causes. The data in each subgroup can be summarized into the average, standard deviation, and sample size. The procedure is described in the following section.

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[20] W. A. Shewhart, *Economic Control of Quality of Manufactured Product,* D. Van Nostrand Co., New York, N. Y. (1931)

[21] N. S. Grant, O. A. Mason and H. F. Donnelly, *Pulp Paper Mag. Canada 48,* No. 3: 151–158, Convention Issue (1947)

[22] C. A. Bicking, *Pulp Paper Mag. Canada 49,* No. 3: 181–188, Convention Issue (1948)

[23] J. G. Strieby, *Paper Trade J. 127,* No. 24: 515–521 (Dec. 9, 1948)

Construction of Control Chart. There are several different ways of expressing the results, but the type of control diagrams originated by Shewhart are the most generally used. The control chart is a simple tool which can be understood by any supervisor. It is helpful because it furnishes a basis for taking corrective action.

Bicking[24] has described in simple and lucid fashion the construction of a Shewhart control chart, using basis weight measurements taken on samples of paper from consecutive reels. The following data and explanation are taken from his work showing how the data on basis weight are handled in both table and chart form. See Tables IV–VIII and Figures XVII-2 to XVII-5 (pages 1001–1002).

The curve in Figure XVII-4 expresses the normal condition of the process or, in other words, the inherent variability of the process. Limits of $\pm 3\sigma$ are used as the control limits although some use 2σ and even 1.5σ for signal points. From this it may be assumed that any average of subgroups of four successive tests which deviate further from the average than the limits ($\pm 3\sigma$) set by the curve is not a chance cause. If a greater variation than this occurs, it is worth while to search for an assignable cause of

TABLE IV

Original Data[24]

These values are listed in order of production
Basis weight, grams per square foot

36	37.5	37.6	34.8
37.2	34.9	36.2	32.2
38	36.0	37	32.8
37.6	37.7	37	31.4
37	36.4	37.7	36.2
36.2	34.5	37.4	33.3
36.8	39	35.4	33.8
36.6	38.6	38.8	37
37.2	38.2	32.8	39.6
36.8	39.0	35.4	33.8
36.6	38.6	38.8	37
37.2	38.2	32.8	39.6

[24] C. A. Bicking, *Tech. Assoc. Papers 30:* 135–139 (June, 1947)

TABLE V

UNGROUPED FREQUENCY DISTRIBUTION[25]
These values are arranged in order of magnitude
Basis weight, grams per square foot

31.4	34.9	36.8	37.6
32.2	35.4	37	37.7
32.8	36	37	37.7
32.8	36	37	38
33.3	36.2	37	38.2
33.5	36.2	37.2	38.6
33.8	36.2	37.2	38.8
34.5	36.4	37.4	39
34.8	36.6	37.6	39.6

TABLE VI

GROUPED FREQUENCY DISTRIBUTION[25]
Values are grouped into different measurement intervals
showing number of values in each interval
Basis weight, grams per square foot

Cell No.	Class intervals	Frequency
1	30.55–31.55	1
2	31.55–32.55	1
3	32.55–33.55	4
4	33.55–34.55	2
5	34.55–35.55	3
6	35.55–36.55	6
7	36.55–37.55	9
8	37.55–38.55	6
9	38.55–39.55	3
10	39.55–40.55	1

TABLE VII

AVERAGES OF SUCCESSIVE GROUPS (4) OF BASIS WEIGHTS[25]
Averages are taken for each successive group of four basis weights from original data.

37.2
36.7
35.4
36.9
37.7
37.3
36.0
33.2
35.7

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[25] C. A. Bicking, *Tech. Assoc. Papers 30:* 135–139 (June, 1947)

TABLE VIII

DISTRIBUTION OF AVERAGES OF SUBGROUPS[25]

Cell No.	Boundaries	Frequency
1	30.55–31.55	0
2	31.55–32.55	0
3	32.55–33.55	1
4	33.55–34.55	0
5	34.55–35.55	1
6	35.55–36.55	2
7	36.55–37.55	4
8	37.55–38.55	1
9	38.55–39.55	0
10	39.55–40.55	0

variation. On the other hand, it is uneconomic to look for a cause of variation if the average of all the subgroups falls within these limits.

If Figure XVII-4 is rotated clockwise, the ends of the curve can be extended as horizontal dotted lines to provide upper and lower control limits, as shown in Figure XVII-5. The final step consists of plotting the subgroup against time, using the above limits as horizontal limits on the curve, as shown in Figure XVII-5. Then, if any value falls outside of these prescribed limits, it can be assigned to some new variation which is causing the system to operate at a new value.

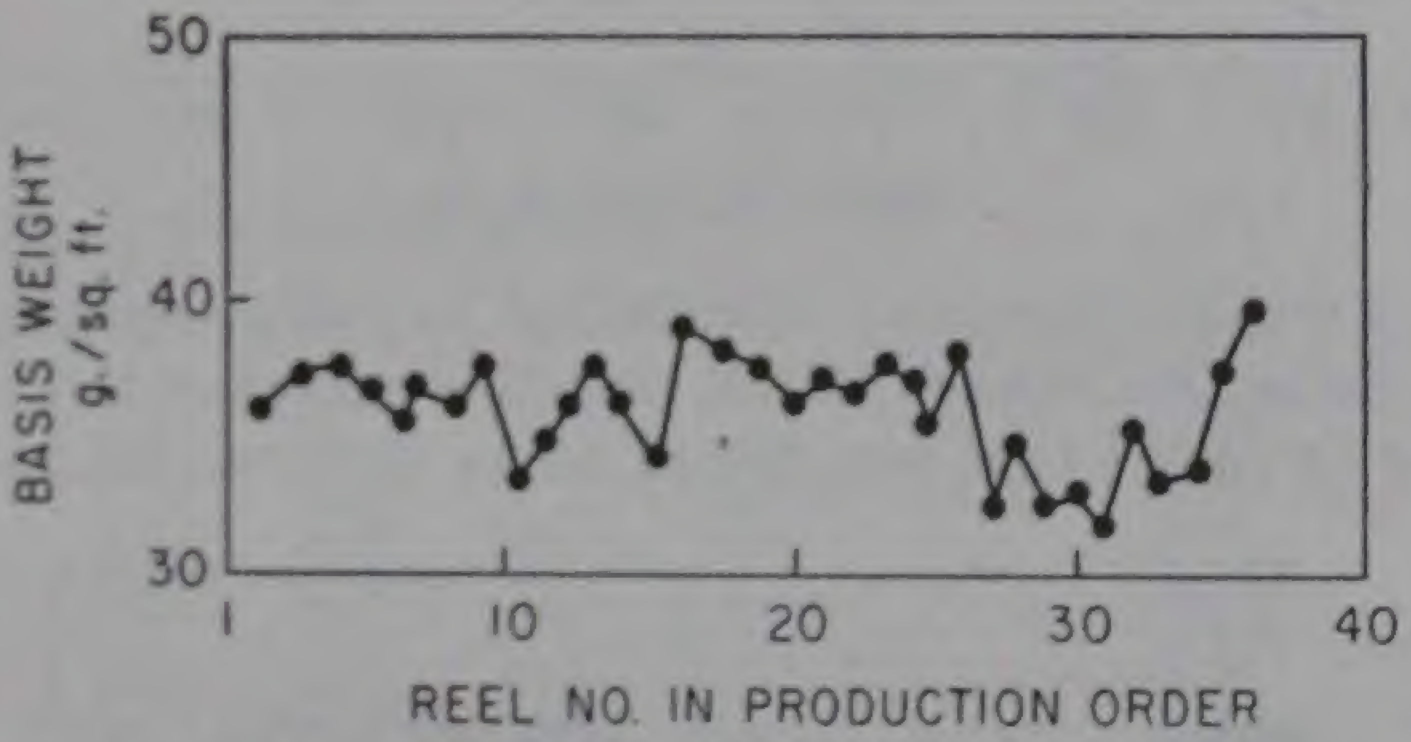

Fig. XVII-2. Data obtained in chronological order.[25]

Use of Formulas for Constructing Control Charts. It is unnecessary to follow all the above steps, since the same results can be obtained by the use of relatively simple formulas which are given in texts on statistics. Formulas are available for two distinct methods of control:

(*1*) Control with respect to a given standard (to determine uniformity of quality). This method requires two sets of formulas and is too confusing for practical control work.

(*2*) Control with no given standard (to determine the constancy of samples).

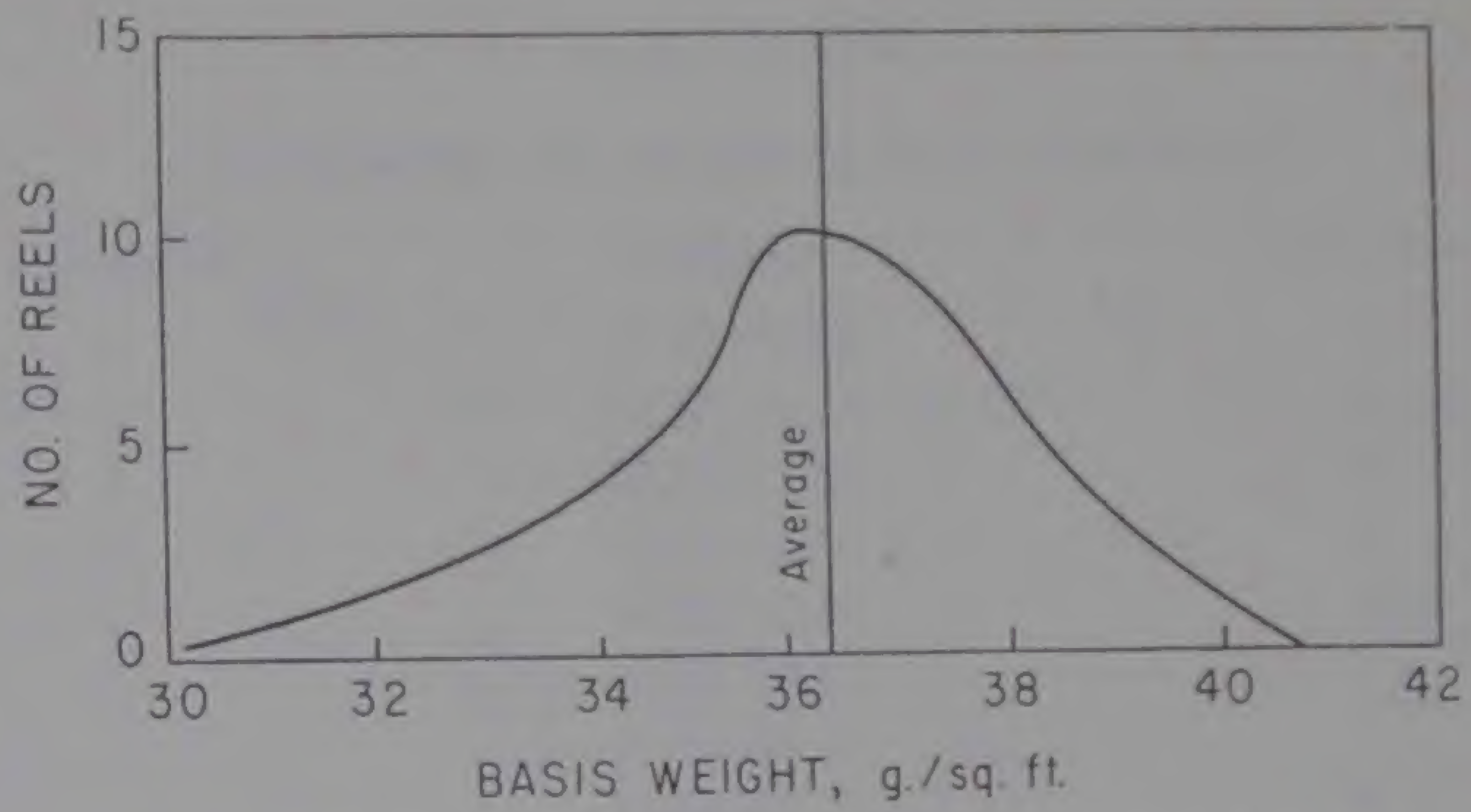

Fig. XVII-3. Frequency distribution curve for individual results.[25] The vertical scale shows the frequency of test measurement at each class interval.

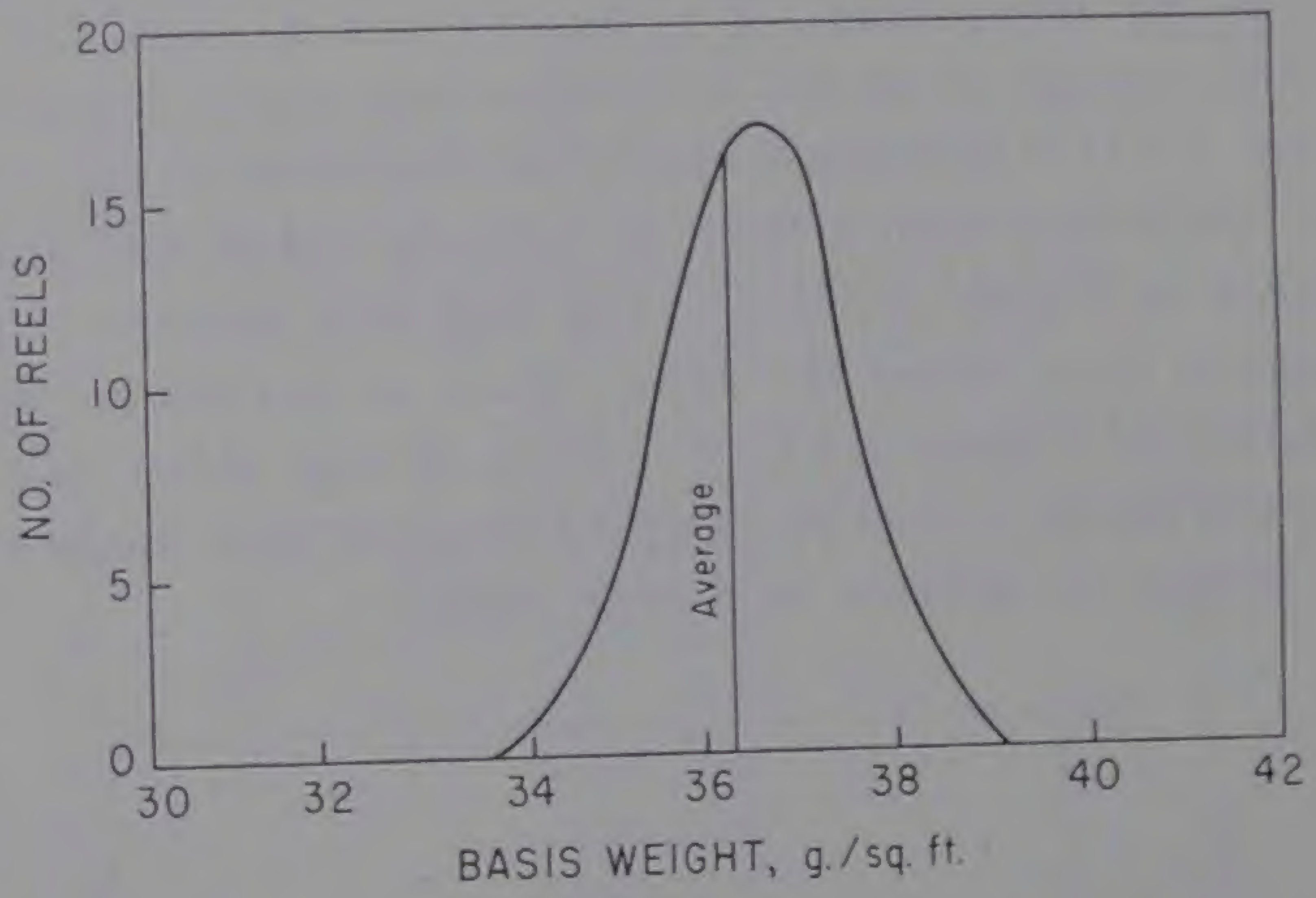

Fig. XVII-4. Frequency distribution for subgroup averages.[25] This is similar to Figure XVII-3 with the exception that the extremes of variability have been ironed out by the grouping procedure.

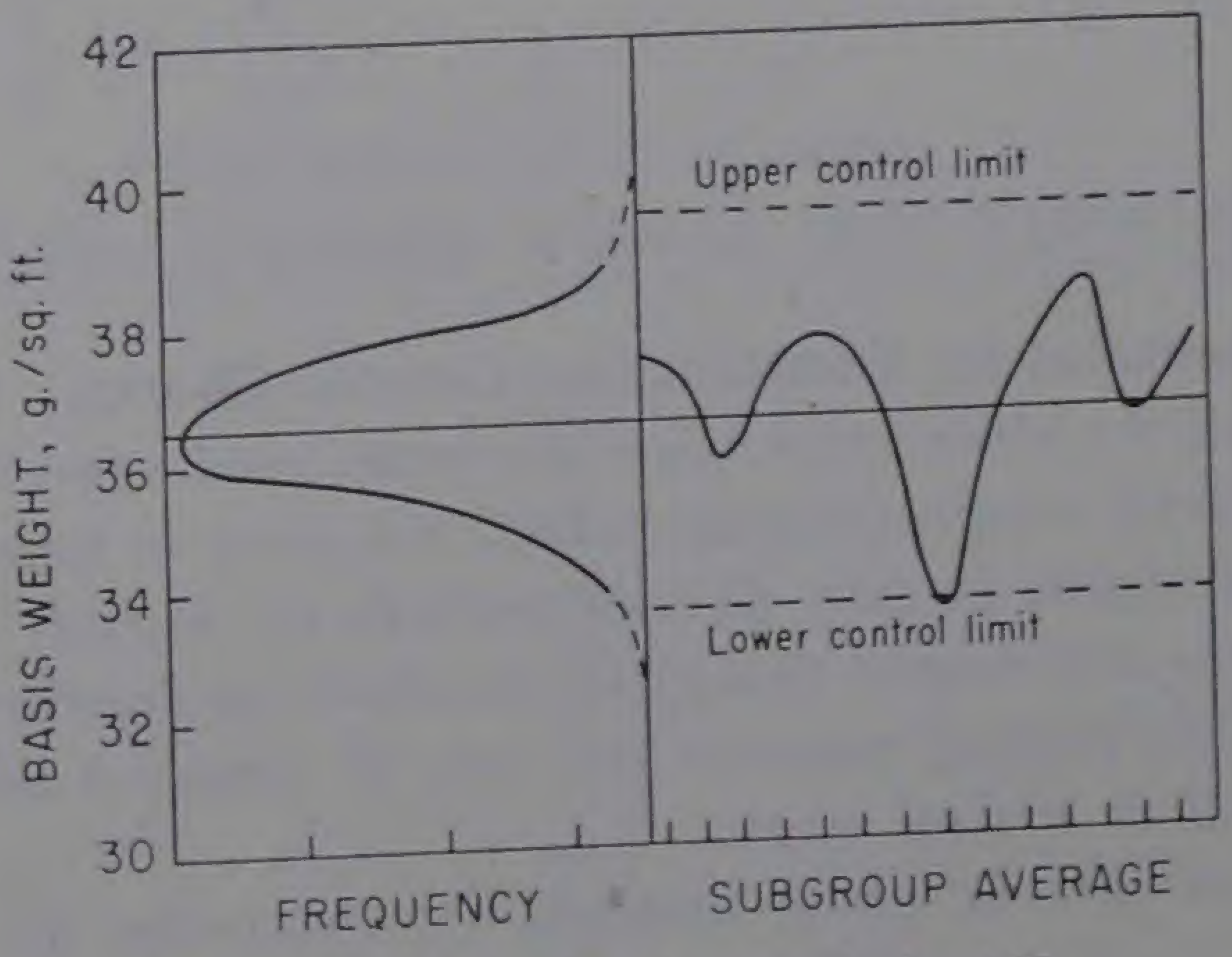

Fig. XVII-5. Final control chart.[25]

For systems where no standard is given, the central line and control limits can be obtained as follows, where n is the number of samples tested. The use of range (R) is so efficient that use of control charts for σ is scarcely ever warranted.

	Control limits		
	Central line	Using factors	Using formulas
Averages using σ	$\overline{\overline{X}}$	$\overline{\overline{X}} \pm A_1\overline{\sigma}$	$\overline{\overline{X}} \pm 3\frac{\overline{\sigma}}{C_2\sqrt{n}}$
Averages using R	$\overline{\overline{X}}$	$\overline{\overline{X}} \pm A_2\overline{R}$	$\overline{\overline{X}} \pm 3\frac{\overline{R}}{d_2\sqrt{n}}$
Standard deviations	$\overline{\sigma}$	$B_3\overline{\sigma}$ and $B_4\overline{\sigma}$	$\overline{\sigma} \pm 3\frac{\overline{\sigma}}{C_2\sqrt{2n}}$
Ranges	$\overline{R}$	$D_3\overline{R}$ and $D_4\overline{R}$	$\overline{R} \pm 3\sigma_R$

The factors A_1, A_2, B_3, B_4, d_2, D_3 and D_4 are obtained from suitable Tables, e.g., Table X which lists the proper values based on the number of items in each of the subgroups.[26, 27]

An example of the use of formulas for calculating control data for averages and ranges is shown in Table IX, based on the data previously analyzed in curve form. The successive sets of four test results are arranged horizontally in subgroups and the mean ($\overline{X}$) and the range (R) are calculated as shown. In this case, no standards are given. $\overline{X}$ is the average of the four measurements in each subgroup. R (range) is the difference between the highest and lowest weight in each subgroup. $\overline{\overline{X}}$ is the

TABLE IX

CONTROL CHART COMPUTATIONS FROM ORIGINAL DATA ON BASIS WEIGHT

Subgroup	Measurement, g./sq. ft.				$\overline{X}$	R
1	36.0	37.2	38.0	37.6	37.2	2.0
2	37.0	36.2	36.8	36.6	36.7	.8
3	37.2	33.5	34.9	36.0	35.4	3.7
4	37.7	36.4	34.5	39.0	36.9	4.5
5	38.6	38.2	37.6	36.2	37.7	2.4
6	37.0	37.0	37.7	37.4	37.3	0.7
7	35.4	38.8	32.8	34.8	36.0	6.0
8	32.2	32.8	31.4	36.2	33.2	4.8
9	33.3	33.8	37.0	39.6	35.7	6.3
Grand average					*36.23*	
Average range						*3.47*

---

[26] E. S. Pearson, "The Application of Statistical Methods to Industrial Standardization and Quality Control," British Standards Inst., London (1935)

[27] *A.S.T.M. Manual on Presentation of Data,* p. 20. Published by the American Society for Testing Materials, Philadelphia, Pennsylvania (1940)

grand average obtained from the averages of each subgroup. $\overline{R}$ is the average range obtained from the averages of each subgroup.

The limits for the averages (mean) were obtained as follows:

$$\overline{\overline{X}} \pm A_2R = 36.23 \pm (0.729 \times 3.47) = 38.76 \text{ and } 33.70 \text{ g./sq. ft.}$$

The limits for ranges were obtained as follows:

$$D_3\overline{R} = 0 \times 3.47 = 0$$
$$D_4\overline{R} = 2.282 \times 3.47 = 7.9 \text{ g./sq.ft.}$$

As just mentioned, the values for A_2, D_3, and D_4 were obtained from Table X.

TABLE X

FACTORS FOR COMPUTING CONTROL CHART LINES—SMALL SAMPLES

Chart for averages		Chart for ranges		
Number of observations in sample, n	Factors for control limits A_2	Factor for central line d_2	Factors for control limits D_3	D_4
2	1.880	1.128	0	3.268
3	1.023	1.693	0	2.574
4	0.729	2.059	0	2.282
5	0.577	2.326	0	2.114
6	0.483	2.534	0	2.004
7	0.419	2.704	0.076	1.924
8	0.373	2.847	0.136	1.864
9	0.337	2.970	0.184	1.816
10	0.308	3.078	0.223	1.777
11	0.285	3.173	0.256	1.744
12	0.266	3.258	0.284	1.717
13	0.249	3.336	0.308	1.692
14	0.235	3.407	0.329	1.671
15	0.223	3.472	0.348	1.652

CENTRAL LINES AND CONTROL LIMITS

	Central line	Control limits
Averages using R	$\overline{\overline{X}}$	$\overline{\overline{X}} \pm A_2\overline{R}$
Ranges	$\overline{R}$	$D_3\overline{R}$ and $D_4\overline{R}$

The various steps in setting up a control chart may then be summarized as follows:

(*1*) Obtain the average of from 15 to 25 sets of test averages for the base period ($\overline{\overline{X}}$).

(*2*) Calculate the upper and lower limits as outlined above.

(*3*) On a suitable chart, draw a line to represent $\overline{\overline{X}}$ and dotted lines to represent the upper and lower control limits.

(*4*) Plot averages on the chart. Also plot ranges between range limits.

All points falling outside the control limits should be investigated by check tests and a search made for assignable causes. All future tests showing any trend toward the control limits should be taken as a sign of approaching trouble. After all assignable causes have been eliminated, a new base period should be established and new control limits set up.

Data to Indicate Relationship

Correlation Coefficient. A problem that frequently arises is the measure of the relation between two variables. One method of measuring the relationship between two variables which vary in *linear* fashion is the correlation coefficient (r), which varies from + 1.0 for perfect positive correlation to − 1.0 for perfect negative correlation. When no correlation

TABLE XI

TABLE OF THE CORRELATION COEFFICIENT

Degrees of freedom	r				
	0.10	0.05	0.02	0.01	0.001
1	0.988	0.997	0.999	1.000	1.000
2	.900	.950	.980	0.990	0.999
3	.805	.878	.934	.959	.992
4	.729	.811	.882	.917	.974
5	.669	.754	.833	.874	.951
6	.621	.707	.789	.834	.925
7	.582	.666	.750	.798	.898
8	.549	.632	.716	.765	.872
9	.521	.602	.685	.735	.847
10	.497	.576	.658	.708	.823
11	.476	.553	.634	.684	.801
12	.457	.532	.612	.661	.780
13	.441	.514	.592	.641	.760
14	.426	.497	.574	.623	.742
15	.412	.482	.558	.606	.725
16	.400	.468	.543	.590	.708
17	.389	.456	.528	.575	.693
18	.378	.444	.516	.561	.679
19	.369	.433	.503	.549	.665
20	.360	.423	.492	.537	.652
25	.323	.381	.445	.487	.597
30	.296	.349	.409	.449	.554
35	.275	.325	.381	.418	.519
40	.257	.304	.358	.393	.490
45	.243	.287	.338	.372	.465
50	.231	.273	.322	.354	.443
60	.211	.250	.295	.325	.408
70	.195	.232	.274	.302	.380
80	.183	.217	.256	.283	.357
90	.173	.205	.242	.267	.337
100	.164	.195	.230	.254	.321

exists, $r = 0$. The coefficient of correlation is calculated as follows:

$$\gamma = \frac{\Sigma(x-\overline{x})\ (y-\overline{y})}{\sqrt{\Sigma(x-\overline{x})^2\,\Sigma(y-\overline{y})^2}}$$

where:

$$\Sigma(x-\overline{x})\ (y-\overline{y}) = \Sigma(xy) - \frac{\Sigma(x)\Sigma(y)}{n}$$

$$\Sigma(x-\overline{x})^2 = \Sigma(x^2) - \frac{(\Sigma x)^2}{n}$$

$$\Sigma(y-\overline{y})^2 = \Sigma(y^2) - \frac{(\Sigma y)^2}{n}$$

To test for significance, the value of r obtained by use of the above formula should be tested to see if it is larger than would have been obtained in the absence of correlation. This is done by comparing the calculated value of r with the value obtained from suitable tables, e.g., Table XI[28] for the proper significance level and degrees of freedom, using $n-2$ for the degree of freedom. If the value of r is greater than that for the proper level of significance, a positive correlation exists; for example, if greater than the value of r at the 0.5% level, there is better than a 19 to 1 chance that there is a real correlation.

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[28] K. A. Brownlee, *Industrial Experimentation*, Chemical Publishing Company, Brooklyn, N. Y. (1947)

CHAPTER XVIII

PIGMENT COATING

Paper coating is an important part of the paper industry. It is a wide field which includes the application of many different types of coatings to the base paper. This chapter is concerned with pigment coating in which an aqueous mixture of pigment and adhesive is applied to the surface of the paper. This type of coating is used primarily for the production of printing papers for magazines and catalogues.

Some of the earliest uses of pigment-coated papers were for wallpapers, box coverings, and other fancy papers. Box coverings were often highly glazed by the flinting process to produce a glossy coating which was usually colored to increase its attractiveness. In contrast, wallpapers were generally dull-finished. At one time, these various types of coatings were probably regarded as separate processes, but today it is customary to group into the class of pigment-coated papers all papers which are coated with a pigment-adhesive composition.

The first use of coated book papers probably dates back to the introduction of the halftone process of printing. It is debatable which came first, the halftone printing process or coated paper, but it is certain that neither one could have been fully developed without the other. Fine halftone printing plates do not reproduce well by the relief process on uncoated paper, even on the smoothest of machine-finished sheets. Coated paper, however, has made it possible to reproduce the finest halftone printings and to control such properties of the paper surface as ink absorbency, ink receptivity, smoothness, gloss, and brightness.

Most of the coated papers are used in printing. If it were not for the demand of coated papers by the printing industry, coating would be of minor importance. As it is, however, the field of coated papers has become one of the most important parts of the paper industry, due to the demand for better printing surfaces on the part of the printer.

Wallpapers and decorative papers have always been coated on one side only. The earliest coated book papers were also coated on one side only, and it was not until 1875 that paper coated on two sides was made.[1]

There are three basic raw materials used in pigment coating: (*1*) the pigment, (*2*) the adhesive used for bonding the pigment, and (*3*) the base paper, or rawstock, to which the pigment is bonded. Each will be taken up separately. The coating mixture is usually prepared by dispersing the pigment and adhesive separately in water and then mixing the two together. The pigments in common use are clay, calcium carbonate, satin white, and titanium dioxide. The principal adhesives used are starch, casein, and certain synthetic resins. The following is an example of a typical coating formula, although widely different formulas can be used: clay, 100 parts by weight; modified starch, 15 to 20 parts by weight. The clay is first dispersed in 60 parts of water containing a dispersing agent. The starch is cooked with 34 parts of water and then mixed with the clay.

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[1] W. B. Wheelwright, *Modern Lithography 10,* No. 7: 47, 49 (July, 1942)

The Coating Process

After the coating mixture has been prepared, it must be applied to the paper in the coating process, which consists of applying the fluid coating mixture to the base paper, smoothing, drying, and calendering the coating. All these are important steps in the coating process and must be carefully carried out in order to obtain a satisfactory coated paper. These steps will be discussed in the following parts of this chapter, but first, the different types of coating processes will be described.

Conventional Coating

Coating is of two types, conventional and machine. Conventional coating is carried out as a separate operation in a coating plant. The coating plant may be part of the paper mill, or it may be operated independently, in which case the raw stock must be purchased from an outside source. Conventional coating was the earliest method of coating, and until recently, was the only method used. Conventional coating has always been a low-speed process designed to make high-quality papers, but because of the competition of machine-coated papers, conventional coating plants have become interested in replacing their old slow-speed coaters with modern high-speed machines. The highest quality coated papers are still produced by conventional coating.

Machine Coating

Machine coating is carried out on the paper machine as an integral part of the papermaking operation. The paper is coated and dried at normal paper machine speeds. Because of its mass production, machine coating made possible for the first time the development of good coated printing papers at low cost. Machine coating was developed primarily to fill the need for cheap mail-order catalogue paper which would reproduce illustrations better than standard uncoated papers. It has been responsible (together with the development of new rapid-setting inks) for a minor revolution in the publication field.

There are two reasons for the low cost of machine-coated papers. First, as just mentioned, machine coating is a high-speed, mass-production process which turns out a large volume at low unit cost. Second, the coating mixture, which is usually made of starch and clay, costs less than an equal weight of fiber (depending, of course, upon the relative price of pulp, coating adhesive, and clay), and since coated papers are sold on a weight basis, this replacement of fiber by an equal weight of cheaper coating material results in a saving in manufacturing cost. The situation with machine-coated paperboards is somewhat different, since board is not sold on a weight basis, and hence the cost of coating must be carried by the board mill or passed on to the consumer in the form of a higher price for the coated board.

Attempts to coat paper on the paper machine date back to 1880 or earlier. Prior to the advent of true machine coating, several processes were developed for surface filling or "washing" the paper surface with pigmented coating mixtures. The application of coating in this way served to fill in the pores of the paper with pigment, but still left the surface in a predominantly fibrous state. The Wheelwright patent[2] granted in 1916 described the addition of pigmented coating mixture at the size press. The Fair process (see Ch. IX) provided for the addition of pigment to the wet sheet on the paper machine wire, but did not include the use of a binder. Coating at the size press was tried in the early days of machine coating, but coating weights were low, on account of the low solids of the coating mixtures used, and the coating had a tendency to soak into the paper, leaving the surface fibers exposed. All these early semi-coating processes used coating mixtures of low solids contents, and hence were limited to the application of very light-weight coatings. In this way they differed from modern machine-coating processes, which can produce heavily coated paper on one or both sides having a smooth surface and excellent printing quality. Usually, the weight of coating applied is between 5 to 8 lb. per side per ream, although heavier coatings up to 18 and 20 lb. are possible.

In machine coating, the coaters are located between drier sections. The wet coated sheet is passed over at least one drier with the coated side away from the drier surface, so that the coating is dried sufficiently to prevent sticking when it comes into contact with the hot drier surface. Passing the sheet over 5 to 6 additional driers completes the drying. Coating may be applied to both sides at once, or each side may be coated separately. If each side is coated separately, the wire or bottom side is usually coated first, the paper passed over 6 to 8 driers to dry that side of the paper, and then the felt side is coated, followed by another 6 to 8 driers.

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[2] H. M. Wheelwright, U. S. 1,195,888 (Aug. 22, 1916) and U. S. 1,258,840 (Feb., 1918)

On certain grades, two applications of coating may be made to one side of the paper.

Coaters for machine coating must have a rugged construction and yet be capable of fine adjustments. They should be located on the same floor as the paper machine and must not be so complicated that they cannot be operated by the regular paper mill crew at regular machine speeds.

Types of Coating Machines

Egan[3] has described ten basic methods of coating: dip, knife, cast, roll, brush, air brush, spray, print, extrude, and strip. All these methods are not in general use for pigment coating. The most important processes are described below. It should be emphasized that many of these coating processes are protected by patents.

Brush Coaters

Brush coating is used exclusively for conventional coating. In conventional brush coating, the coating is applied by means of a round brush, spatter brush, felt-covered applicator roll, felt blanket, or by dipping the sheet. The round brush is the most satisfactory method. Felt-covered rolls and felt blankets are often used, but the felt tends to fill up with coating and become hardened. Small driven doctor rolls may be used to remove excess coating, after which the coated paper is passed under several sets of reciprocating hair brushes of graduated fineness, which spread the coating evenly over the surface of the sheet. In some installations, a brush is located so that it acts on the sheet as it passes around the head roll. The sheet may be supported by a cylinder or by a rubber blanket at the point where the brushes act on the coating. The first brushes coming into contact with the paper have the coarsest bristles, the greatest amplitude, and the lowest frequency to their vibrations. The cycles on the various brushes are so adjusted that they are out of phase with each other. After the coating is smoothed, the sheet is passed over an air floater which supports the paper and prevents the wet coating from coming into contact with any hard surface until it is partly dried. For paper which is coated on one side only, no air floater is required. The sheet is dried, either in festoon driers or drying ovens. Finally, the coated paper is wound into rolls and calendered in a separate operation.

Brush coating is a slow-speed process which has not been changed since its original development, and is more of an art than a science. Production speeds are limited to about 400 f.p.m. because of the reciprocating brushes used. In a standard brush coating, from 9 to 20 lb. of coating (per ream 25 × 38—500) are usually applied to each side of the paper.

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[3] F. W. Egan, *Paper Trade J. 121,* No. 17: 163–169 (Oct. 25, 1945)

The coated paper is mostly of high quality; it is generally graded into firsts, seconds, and thirds.

Roll Coaters

For many years, brush coaters were the only type of coating machine, but with the advent of machine coating, many new types of coating machines were developed. Among the most important of these are the roll coaters in which coating mixture is applied and spread on the surface of the paper by means of rubber-covered metal rolls. Roll coaters are used mostly for machine coating, although they can be used for conventional coating.

There are two principal types of roll coaters, the planographic and the gravure. These coaters can handle coating mixtures of higher viscosity than can be satisfactorily handled by brush coaters, which permits the use of coating mixtures of high solids content. Modified starches are particularly well suited as the adhesive for the roll coating process. Low-viscosity modified starches have made possible coating mixtures up to 55 to 70% solids, which are about ideal for coating on the paper machine. On the other hand, casein has not been used to any extent for roll coating operations because it must be used at low solids, which leads to an excessive drying load on the machine and a tendency for the coating to stick to the driers. Most machine coating with roll coaters is done with coating mixtures of 58 to 62% solids. Much has been learned about the fundamentals of coating from the operation of high-speed roll coaters. The knowledge gained from roll coating has been of great value in understanding other coating processes.

Planographic Roll Coater. One of the most important of the roll coaters is the planographic coater, of which there are several designs. One design consists of a fountain roll, a series of small, smooth distributing and oscillating rolls, and a smooth print roll. The rolls are alternating chrome and rubber covered. The coating is picked up by the fountain roll and worked between the distributing rolls which meter and distribute the coating and transfer it to the print roll from which it is applied to the paper. Another design consists of two metering rolls and a rubber-covered print roll. One of the metering rolls is chrome plated and the other is a rubber covered roll.

Another coater is somewhat similar except there are two systems of rolls which split the coating and then recombine it just before printing on the paper. The amount of coating mixture applied to the paper can be regulated by the setting between the rolls or by the relative speed of the rolls. The print roll turns in the same direction as the paper travels.

Rotogravure Roll Coater. The rotogravure-offset coater consists of a soft rubber feed roll, a knurled or an engraved roll, a doctor blade, a rubber-covered offset roll, and a backing roll of cast iron or hard rubber. The feed roll revolves in the coating pan where it picks up the coating mixture and applies it to the knurled roll. The excess coating is removed from the knurled roll by means of the doctor blade. The coating may be printed directly on the paper from the knurled roll, or it may be transferred first to an offset roll and then to the paper. An offset roll is beneficial in removing the design or pattern which the knurled roll tends to leave on the paper, and hence results in a smoother coating. The feed roll is driven separately at slow speed, and the knurled roll and offset roll are driven at the same surface speed as the paper. A drawing of an offset rotogravure print coater is shown in Figure XVIII-1.

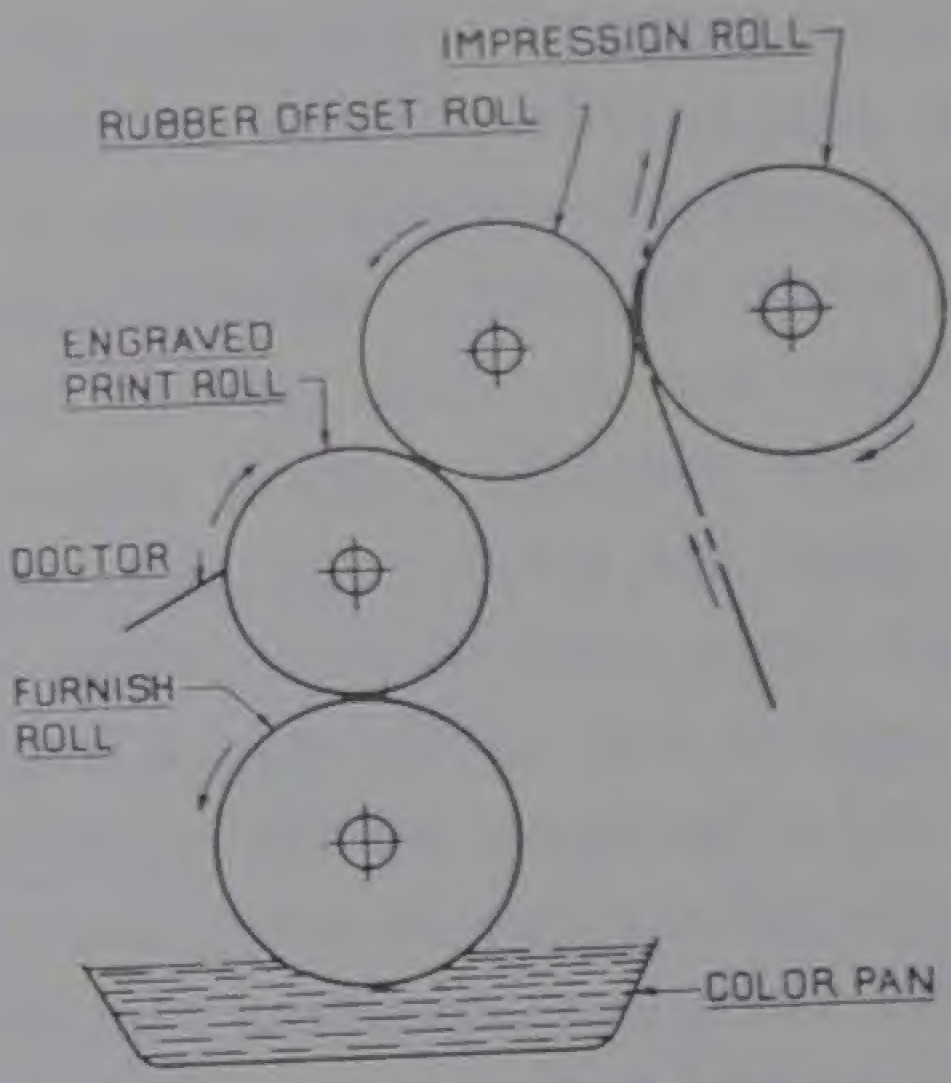

Fig. XVIII-1. Diagram of an offset rotogravure print coater (courtesy John Waldron Corp.).

When the coating is first picked up by the offset roll, it is in the form of discontinuous areas corresponding to the recessed areas on the knurled or engraved roll, but these areas tend to flow together into a continuous film on the surface of the offset roll. When the coating is transferred to the paper, the film splits, with most of the film sticking to the paper, but a part staying with the offset roll. This film-splitting accounts for the ribbed texture in the coating.

It is difficult to vary the weight of coating applied to the paper with gravure coaters. The only method of changing the weight of dry coating applied to the paper with this type of coater is by changing the per cent solids of the coating mixture, since the volume of coating mixture applied is predetermined by the engraving on the print roll. With knurled rolls, the ratio of cup area to wall area is usually fixed at slightly over 2 to 1,[4] and the solids content of the coating mixture must be adjusted to apply the correct amount of coating under these conditions. If the coating weight is to be changed, the solids content will have to be adjusted (or the roll changed).

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[4] G. Haywood, *Paper Trade J. 127,* No. 3: 314–316 (July 15, 1948)

The viscosity of the coating mixture used in gravure coating must be controlled in order that coating will distribute well without producing a pattern on the paper. Too low a viscosity causes flooding of the nip between the knurled roll and the offset roll, whereas too high a viscosity prevents proper flow or spreading of the coating on the offset roll. The viscosity also affects the amount of coating transferred to the paper. However, the proper viscosity is determined by the working properties of the coating mixture on the rolls and cannot be changed from the optimum point to control the amount of coating applied.

Knife Coaters

Knife coaters are used for machine coating, primarily for the coating of paperboard. In the knife coater, an excess of coating is applied to the paper by means of a roll revolving in a pan of the coating mixture, and the excess coating is then removed and the remaining coating is smoothed by passing the paper underneath a stationary knife blade. An important factor in knife coating is the draw or tension on the sheet, since the amount of this tension determines the pattern of the coating and the amount applied. A sheet which is run loose will receive more coating, but the pattern will not be so good as a sheet which is run with a tight draw. The draw can be readily adjusted, since the coater is generally located between drier sections. The coated paper has a moisture content of about 40 to 50% when it goes to the driers.[5, 6]

In addition to the straight-edge knife coater, there is also the Mayer type coater in which a small revolving rod is used in the knife edge. This rod is wound with wire, the size of which determines the amount of coating spread on the paper.

Another special type of knife coater, which is in the early stages of commercial use, consists of a pneumatic diaphragm which supports the paper as it passes under a straight-edge knife. Low air pressure is maintained in the diaphragm to level out the surface of the paper and furnish a resilient support.

Casein is the principal adhesive used in knife coating, and some synthetic latex is often used with casein to improve the flexibility of the coating. The amount of coating applied varies from about 1 to 4 lb. of coating per 1,000 sq.ft. The base paper for knife coaters must be exceptionally smooth and possess a high degree of internal strength. Beater starches are frequently used in the base paper for strengthening the surface. It is desirable to use finely woven felts on the paper machine to keep the surface of the paperboard as smooth as possible.

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[5] J. R. Simpson, *Paper Trade J. 128,* No. 13: 109–111 (Mar. 31, 1949)

[6] *Paper Trade J. 128,* No. 12: 12–13 (Mar. 24, 1949)

Air Brush Coaters

Another type of coater is the air brush or air knife coater. In this coating process, an excess of coating is applied to the paper by roll applicator, and the excess coating is then blown off the sheet by means of a thin air jet which strikes the wet coating at an angle where the sheet is wrapped around a breast roll. The air jet can be regulated for velocity and width of stream in order to regulate the amount of coating left on the paper. The velocity of air leaving the air doctor varies from 20,000 to 40,000 f.p.m., depending upon the pressure used. The excess coating is removed in the form of small drops which are separated from the air by baffling and by loss of velocity of the air. This coating is collected in pans, returned to the supply tank and recirculated. The excess coating removed from the paper amounts to about 30 to 50% of the original coating applied to the paper. There are two commercial air knife coaters, the Warren air knife and the Microjet.

Air brush coaters produce a uniform coating even on papers having a very rough surface (e.g., wallpaper stock). They cannot be used for coating heavy boards which are too stiff to be wrapped around the breast roll. The coater is used for both conventional and machine coating.

The properties required in a coating mixture for air knife coating are approximately the same as those required for brush coating, with the exception that coating mixtures of a wider range of viscosities can be handled. There is some tendency for air brush coaters to classify the pigment in the coating mixture, resulting in a build-up of the larger particles. However, this difficulty can be eliminated by better dispersion of the pigment and the use of pigments of finer particle size.

Coating Adhesives

The adhesive exerts a profound influence on the properties of the coating mixture and the properties of the final coated paper. The functions of the adhesive in pigment coating are as follows: (*1*) to serve as a carrier for the pigment so that the coating mixture will have the proper flow properties; (*2*) to bond the pigment particles together in the dried coating and to bond the pigment to the body stock; (*3*) to control the absorption of printing ink during printing of the coated paper.

Properties Necessary in Coating Adhesives

An adhesive, to be satisfactory, should have a high pigment bonding strength and good color. Moreover, the adhesive should not obscure the properties of the pigment, but should produce with the pigment a surface that is highly receptive to printing ink. The adhesive must have the correct viscosity for the solids content at which the coating mixture is to be used and should have strong filming properties to prevent excessive penetration of the coating mixture into the raw stock at the time of coating. The adhesive should be compatible with the pigment and should produce a coating mixture with a high degree of colloidal stability, so that the properties of the coating mixture do not change during the period of use. Finally, the adhesive should have enough plasticity so that the coating will not powder or dust during calendering.

The most important single property of the adhesive is the pigment bonding strength, because this property determines the amount of adhesive required to hold the pigment on the paper. Each grade of coated paper has a fairly definite strength requirement, and the amount of adhesive necessary in the coating mixture to meet this requirement is determined by the pigment bonding strength of the adhesive. The pigment bonding strength of the adhesive indirectly affects all the properties of the coating, because the amount of adhesive in the coating affects the opacity, brightness, color, and smoothness, as well as the strength. If the ratio of adhesive to pigment is excessive, the quality of the coating will be poor, from a printing standpoint.

The pigment bonding strength of the adhesive is determined by (*1*) the cohesive strength between the adhesive molecules and (*2*) the adhesive bond formed between the adhesive, the pigment, and the raw stock. In this respect, pigment coating is related to the fundamental laws governing all adhesive action, although pigment bonding is more complicated than most adhesive problems.

The earliest adhesives used in pigment coating were animal glue and gum arabic; later, casein was widely used. Today, the principal adhesives are starch, casein, and soybean protein. Most of the casein is used in conventional coating, and most of the starch in machine coating. Other adhesives used in lesser amounts are polyvinyl alcohol, water-soluble cellulose derivatives, synthetic latices, and soy flour. The properties of the various adhesives and the methods of preparation of various adhesive solutions are discussed in the following sections.

Casein

Casein was the most important adhesive used in pigment coating prior to the advent of machine coating, after which starch became increasingly important. Casein is still an important adhesive for the coating of high-grade papers or papers in which a high degree of water resistance is desired. Most of the casein is used in conventional coating with brush coaters or air knife coaters, although some casein is used for machine coating particularly by the knife coating process.

Casein is a by-product of the dairy industry and is prepared from skim milk by coagulation in the form of a curd. About 2½ lb. of casein are obtained from 100 lb. of milk. Casein in milk is combined with calcium and is associated with some calcium phosphate in the form of colloidal complexes which are suspended in an aqueous solution of lactose and mineral salts. Hydrochloric acid, lactic acid (from natural souring), and rennet are the common coagulating agents used for the separation of casein from milk. The properties of casein depend somewhat upon the coagulating agent used. In acid coagulation, the *p*H of the milk is lowered to the isoelectric point of the casein (*p*H 4.6–4.7) with hydrochloric acid. In the natural souring method, the milk is held in vats at a temperature favoring fermentation until sufficient lactic acid is formed to coagulate the casein. Rennet (obtained from cows' stomachs) is used as the coagulant in the other important process. Since rennet coagulates casein best at a *p*H around 6.0 to 6.4, the casein is less hydrolyzed than acid casein. After coagulation, the curd must be washed to remove free acid, sugar, and mineral salts. A high ash content is an indication that the casein has been poorly washed. The final step is drying of the casein, and care must be taken to avoid excessively high temperatures, since this forms a case-hardened product which is difficult to dissolve.

Casein is a relatively non-uniform product, unless it is carefully blended. Blending is customary with the large distributors. Both domestic and imported (mostly Argentinian) caseins are used. In Europe, French casein is considered the best. All the different types of caseins (acid, rennet, and self-sour casein) have been used in pigment coating, although each type seems to work somewhat differently.[7]

Casein arrives at the mill either as a crude dried curd or as a coarsely ground powder. Excessively fine particles are undesirable because they increase the difficulty of wetting, and because they appear to be associated with excessive foaming. Milham[8] gives the desirable fineness rule that all the casein should pass a 10-mesh screen, and not more than 10% should pass a 40-mesh screen. An approximate analysis of casein is given below:[9]

Carbon	53.5%
Hydrogen	7.13%
Nitrogen	15.8%
Sulfur	0.72%
Phosphorus	0.71%
Moisture	5.5–10.5%
Ash	1.5–4.5%
Fat	0.2–2.5%
Specific gravity	1.25 to 1.31

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[7] E. O. Whittier, S. P. Gould, R. W. Bell, M. B. Shaw and G. W. Bicking, *Ind. Eng. Chem. 25,* No. 8: 904–908 (Aug., 1933)

[8] E. G. Milham, *Paper Trade J. 103,* No. 1: 23–24 (July 2, 1936)

[9] L. L. Van Slyke and A. W. Bosworth, *J. Biol. Chem. 14:* 203 (1913)

Casein always contains some fat. Excess fat causes trouble with grease spots in the coated paper, but up to 2.25% fat can be present without causing trouble.[10]

Casein should always be stored in a dry place, but not where it is excessively dry, since this lowers the moisture content and reduces the solubility.[11] Casein is likely to become infested with weevils or worms on storage. Casein infested in this way dissolves more readily (often requiring only 40 to 50% of the normal amount of alkali), but the pigment bonding strength of infested casein is greatly reduced (sometimes being only 50% that of uninfested casein).

When casein is stirred into water, the individual granules imbibe water and swell, but do not dissolve unless the medium is highly alkaline or highly acid. Alkali and heat are generally used for dispersing casein in pigment coating. About 5 to 6 parts of water are used for each part of casein. The casein should be soaked in cold water for at least fifteen to thirty minutes and stirred during this period in order to swell the casein curd and permit subsequent penetration of the alkali. The alkali is dissolved in a small amount of remaining water and is added to the thoroughly wetted casein while agitating, after which the suspension can be heated to 130 to 140° F. and held there for fifteen to thirty minutes, or until the casein is completely dispersed.

The type of alkali used is very important. Sodium, potassium, and ammonium hydroxides are more rapid solvents than the weaker alkalies such as borax and trisodium phosphate. The hydroxides of alkali metal earths, e.g., calcium and magnesium hydroxides, are slower solvents than the sodium and potassium hydroxides and are not generally used because of their tendency to flocculate pigments used in the coating mixture. Caustic soda reputedly produces denser and clearer films than other alkalies, although the films are somewhat more brittle. Milham[12] reports that sodium carbonate produces a fairly clear and tough film, although the film has relatively poor varnishing properties; it tends to produce a foamy dispersion, unless a large excess of alkali is used, or unless it is used in combination with ammonia or some other alkali. The phosphates and silicates give somewhat porous films having relatively poor varnishing properties. Ammonia produces a fairly dense and tough film which has a good bonding strength and readily lends itself to waterproofing; if ammonia is used, it should be added at the end of the heating period.

The amount of alkali required for dissolving casein is greater than the stoichiometric amount, because considerable alkali is adsorbed on the surface of the casein micelles.[13] The amount of alkali depends somewhat upon the type of pigment with which the casein is to be used. For example, less alkali is required when satin white is used as the pigment than when clay is used. Mixed alkalies are frequently used for dissolving casein. A few typical formulas are given in Table I.

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[10] E. O. Whittier, S. P. Gould, R. W. Bell, M. B. Shaw and G. W. Bicking, *Ind. Eng. Chem.* 25, No. 8: 904–908 (Aug., 1933)

[11] W. E. Stringer, *Paper Trade J.* 110, No. 11: 160–162 (Mar. 14, 1940)

[12] E. G. Milham, *Tappi Bull.* 57 (Aug. 6, 1945)

TABLE I

TYPICAL FORMULAS FOR DISSOLVING CASEIN FOR PIGMENT COATING

Fomula 1	Formula 2	Formula 3	Formula 4
100 parts casein	100 parts casein	100 parts casein	100 parts casein
8 parts sodium carbonate	10 parts sodium carbonate	5 parts sodium hydroxide	8 parts ammonia (26° Bé.)
8 parts borax	3 parts ammonia (26° Bé.)		
600 parts water	550 parts water	550 parts water	600 parts water

Too much alkali should not be used in dissolving casein, particularly if the stronger alkalies (e.g., sodium hydroxide) are used, since this brings about rapid decomposition of the casein. Casein solutions made in the cold usually have greater adhesive strength than those prepared by heating because of the greater hydrolysis that takes place under the influence of heat. Casein solutions having a *p*H of 10.5 or above are subject to rapid decomposition. Most casein coating mixtures have a *p*H between 9.0 and 10.0, and even at room temperature casein will hydrolyze slowly at this *p*H, with a resulting breakdown of the casein into ammonia and other decomposition products. Thus, casein coating mixtures cannot be held indefinitely, even though protected from spoilage with preservatives.

Casein produces relatively viscous solutions compared with most other coating adhesives; the viscosity increases rapidly with increasing concentration. Casein solutions exhibit truly viscous flow at a concentration of 9% solids, but are pseudoplastic at a concentration of 12% solids.[14] Increasing the temperature lowers the viscosity, and prolonged heating of casein solutions results in a permanent reduction in viscosity, particularly if the *p*H is very high. The high viscosity and tendency toward plastic flow makes casein undesirable for certain paper coating processes.

The conventional manner of using casein has been to dissolve with alkali and then add the casein solution to a separately prepared mixture of pigment and water. However, newer methods have been developed which produce coating mixtures of lower viscosity and other more desirable flow properties.[15] In one procedure, dry casein is added to the pigment-water

[13] *J. Phys. Chem.* 29: 769 (1925)

[14] R. W. Bell and S. P. Gould, *J. Dairy Sci. 14:* 337 (1931)

[15] J. W. Smith, R. T. Trelfa and H. O. Ware, *Tappi 33,* No. 5: 212–218 (May, 1950)

mixture and solubilized in the presence of the pigment. In another procedure, casein is dissolved in water at 25 to 30% concentration, using 3 to 5% sodium hydroxide on the weight of the casein and a temperature of 110 to 125° F. for twenty to thirty minutes, after which the dry pigment is added. Sodium sesquisilicate is added later to reduce the viscosity.

Casein has a high pigment bonding strength when properly dispersed. A curve showing the relative bonding strength of a number of different adhesives is shown in Figure XVIII-2. This curve shows the amount of dry casein (in comparison with other adhesives) required for each 100 lb. of dry clay in order to obtain a coating which will not pick at various Dennison waxes. About 12 parts of casein will bond 100 parts of clay for most grades of coated printing papers.

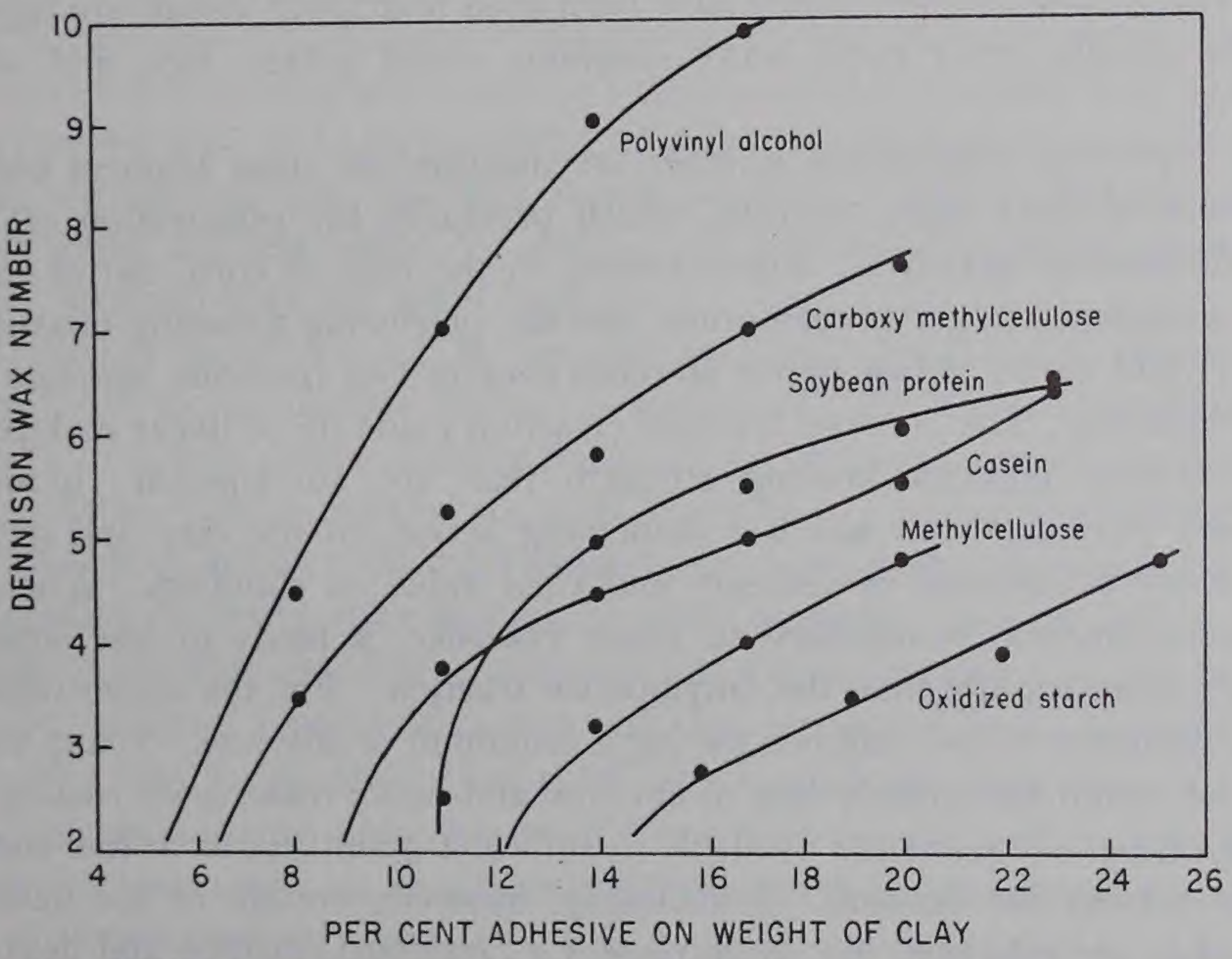

Fig. XVIII-2. Comparison of adhesives for pigment bonding strength.

The particular advantage which casein has over most other adhesives is the ease with which its film can be made water-resistant. Treatment of a dry or semi-dry casein coating with formaldehyde, alum, acids, or lime will produce a highly water-insoluble coating. It is also possible to add formaldehyde directly to the casein coating mixture if it is added in very dilute solution under vigorous agitation. Mixing ammonia with the formaldehyde before adding to the coating mixture will reduce the coagulating effect of the formaldehyde on the casein. Small amounts of formaldehyde added to the coating mixture do not produce an immediate waterproofing of the dried film, but water resistance develops slowly with time.

A qualitative test for casein in coated papers can be made by boiling the paper in 1% caustic soda solution, neutralizing the filtered extract, and treating with Millon's reagent (mercury dissolved in nitric acid). The appearance of a red color on heating indicates the presence of casein. A quantitative test for casein can be made by the Kjeldahl determination.

Starch

Starch has become the most widely used coating adhesive because of its low cost and good working qualities. The introduction of machine coating was responsible for the wide acceptance of starch. Starch can be used to prepare high solids coatings which are particularly well adapted to the demands of machine coating. Most of the starch used is domestic corn starch. Other starches which have been used to a lesser extent are tapioca, white potato, waxy corn, waxy sorghum, sweet potato, rice, and wheat starch.

Native or unmodified starches are unsuited for most pigment coating because of their high viscosity, which precludes the preparation of high solids coating mixtures. Furthermore, in the case of corn, native starch has a tendency to gel or retrograde, thereby producing a coating mixture of high yield value. Most native starches contain two fractions, amylose and amylopectin. The amylose fraction (fraction made up of linear molecules) has greater pigment binding strength than the amylopectin (branched chain) fraction,[16] but has less dispersing action on the clay and greater tendency to increase in viscosity and yield value on standing. When the amylose fraction is modified to lower viscosity, it tends to lose strength much more rapidly than the amylopectin fraction. For the above reasons, it is desirable to use starches having a minimum of amylose. Waxy varieties of starch are entirely free of amylose and hence make good coating adhesives, but these are not available in sufficient quantities or at low enough cost to meet the demand. Fortunately, however, certain of the modified starches are relatively low in amylose, e.g., oxidized starches and dextrins.

Most coating is done with high solids coating mixtures, and hence modified starches of relatively low viscosity are required. However, it should be pointed out that all modified starches tend to lose strength as the modification is carried to products of lower and lower viscosity. This loss in strength depends somewhat upon the type of modifying agent used; each type of modifying agent has definite limitations beyond which it is not practical to reduce the viscosity without causing a serious loss in strength. The principal types of modified starches used for coating are dextrins (from corn), oxidized starches (from corn), and enzyme-converted starches (from corn or tapioca). Modified starches made by acid hydrolysis have a relatively high amylose content and tend to produce coating mixtures of high plasticity and low strength; hence, they are not widely used for paper coating, although they find application in certain special coating processes. (These starches are prepared by hydrolyzing starch in water slurry using mineral acids. They are commonly referred to as thin-boiling starches.) In the early part of 1900, the use of starch acetate (Feculose) was tried out in England, but although it was quite successful at that time, it is not used today because it is no better than the cheaper oxidized starches.

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[16] R. W. Kerr and N. F. Schink, *Paper Trade J. 120,* No. 8: 77–80 (Feb. 22, 1945)

There are three principal types of dextrins, white dextrins, canary dextrins, and British gums. All are made by roasting dry starch, but white dextrins are made with relatively high percentage of acid and low temperature, whereas British gums are made without acid, using high temperatures and long converting periods. Canary dextrins are intermediate to white dextrin and British gums in the amount of acid and heat used. Dextrins are used in coating when coating mixtures of exceptionally high solids are required, e.g., 60 to 70% solids. Highly converted dextrins have the lowest viscosity of any modified starch product. Canary dextrins and British gums are best suited for coating, since they have higher pigment binding strength than the white dextrins.

Oxidized starches used for coating are made by treating starch in slurry form, using alkaline sodium hypochlorite. Oxidized starches are available in a wide range of viscosity but, in general, only the highly modified products of low viscosity are used in coating. Oxidized starches are not available in as low a viscosity range as dextrins, and hence cannot produce coating mixtures quite so high in solids content. One particular advantage of oxidized starches is their natural dispersing effect on pigments (similar to that of casein); this, however, has become of lesser importance since the introduction and widespread use of inorganic dispersing agents (e.g., polyphosphates) which has made the dispersing action of the adhesive of minor importance. At one time, oxidized starches were about the only type of modified starch used for coating. They are still used to a large extent for both machine coating and conventional coating.

Coating starches are generally cooked before being mixed with the pigment. This is done by stirring the starch in the required amount of water and heating to a temperature of about 200 to 212° F. and holding it there for ten to fifteen minutes. Heating and agitation tend to reduce the viscosity of the cooked solution, but the solution should be well agitated during preparation to help stabilize the viscosity. After cooking, the starch solution can be cooled before being added to the pigment slurry if a jacketed tank is used. If the tank is not jacketed and steam is injected directly into the starch during cooking, it is possible to withhold part of the water at first and add it at the end to aid in cooling. Best results are obtained with some modified starches if the starch solution is mixed with the pigment at a temperature of about 140° F. One process[17] calls for cooking the starch in the presence of the pigment. The strength of the coating is increased by 1–2 Dennison waxes by this method, but there is the obvious disadvantage of having to cool the entire batch of starch and pigment.

The general procedure for converting starch with enzymes has been discussed in Chapter XI. The same procedure is used for converting starch for coating, except that the conversion is carried out at higher concentration, and consequently higher percentages of enzyme are required. If the starch is to be used for high solids coating mixtures, approximately 1 to 2% enzyme will be required. (The exact amount depends upon the type of enzyme; the newer enzyme concentrates can be used in much lower concentration.) Enzyme activity is a function both of time and temperature. Enzymes, however, vary in their response to time and temperature variation. Certain enzymes depend mostly on time of conversion (doubling the conversion time results in twice as much conversion), whereas other enzymes lose activity after a short converting period. Certain enzymes result in a progressive loss in strength of the starch as the viscosity is decreased, whereas other enzymes convert starch over quite a range of viscosity without appreciable loss in strength. The effect of degree of enzyme conversion on the viscosity and adhesive strength of corn starch is shown in Figure XVIII-3. In these experiments, starch solutions converted with various percentages of enzyme were made into coating mixtures with clay, the coating applied to paper, and the strength of the resulting coating measured by means of the wax pick test. It is to be noted that both the viscosity of the starch and the adhesive binding strength are lowered as the degree of conversion by enzyme is increased. The loss in binding strength is essentially linear whereas the decrease in viscosity is essentially exponential.[18]

When converting corn starch with enzymes, it is generally better to use low percentages of enzyme and relatively long converting periods, rather than high percentages of enzyme and short converting periods. The reason for this is that all starch granules do not convert at the same rate, and it is desirable to convert relatively slowly in order to obtain the most uniform conversion. As a general rule, starch which has been converted slowly will have greater adhesive strength than starch which has been converted rapidly. Certain enzymes are more heat-resistant than others, and ordinary temperatures are not enough to inactivate completely the enzyme at the end of the converting period. In such cases, chemical inactivation must be used in combination with heat. There are a number of chemicals which can be used to inactivate enzymes, some of which are phosphates, silicates, acids, acid salts, copper sulfate, sodium chlorite, mercury compounds, and formaldehyde. Iron salts are not particularly detrimental to enzyme activity.

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[17] H. T. Ruff, U. S. 2,140,394 (Dec. 13, 1938)

[18] D. A. Hughes and W. L. Craig, *Tappi 33*, No. 5: 253–256 (May, 1950)

One process[19] calls for converting starch with enzyme in the presence of the pigment in a definite and predetermined time cycle and at a constant rate of agitation. With this process it is possible to convert at high solids content without running into excessive thickening of the starch, the whole process being controlled automatically. The resulting product has a higher pigment bonding strength compared to starch converted in the regular manner. When using this process, the *p*H of the starch-pigment-enzyme mixture must be adjusted to between 6.5 to 7.0 during conversion. The conversion can then be carried out in the normal manner by heating to approximately 160° F. and holding there for fifteen to thirty minutes. At the end of the converting period, the entire mixture must be heated to at least 200° F. to cook the starch and destroy the enzyme (this imposes a problem in cooling the batch). Some clays have a tendency to adsorb the enzyme and prevent its action on the starch. Why some clays work well and others do not has not been determined, but the difficulty can be overcome in most cases by adding a small amount of protein or sodium silicate to the clay be-

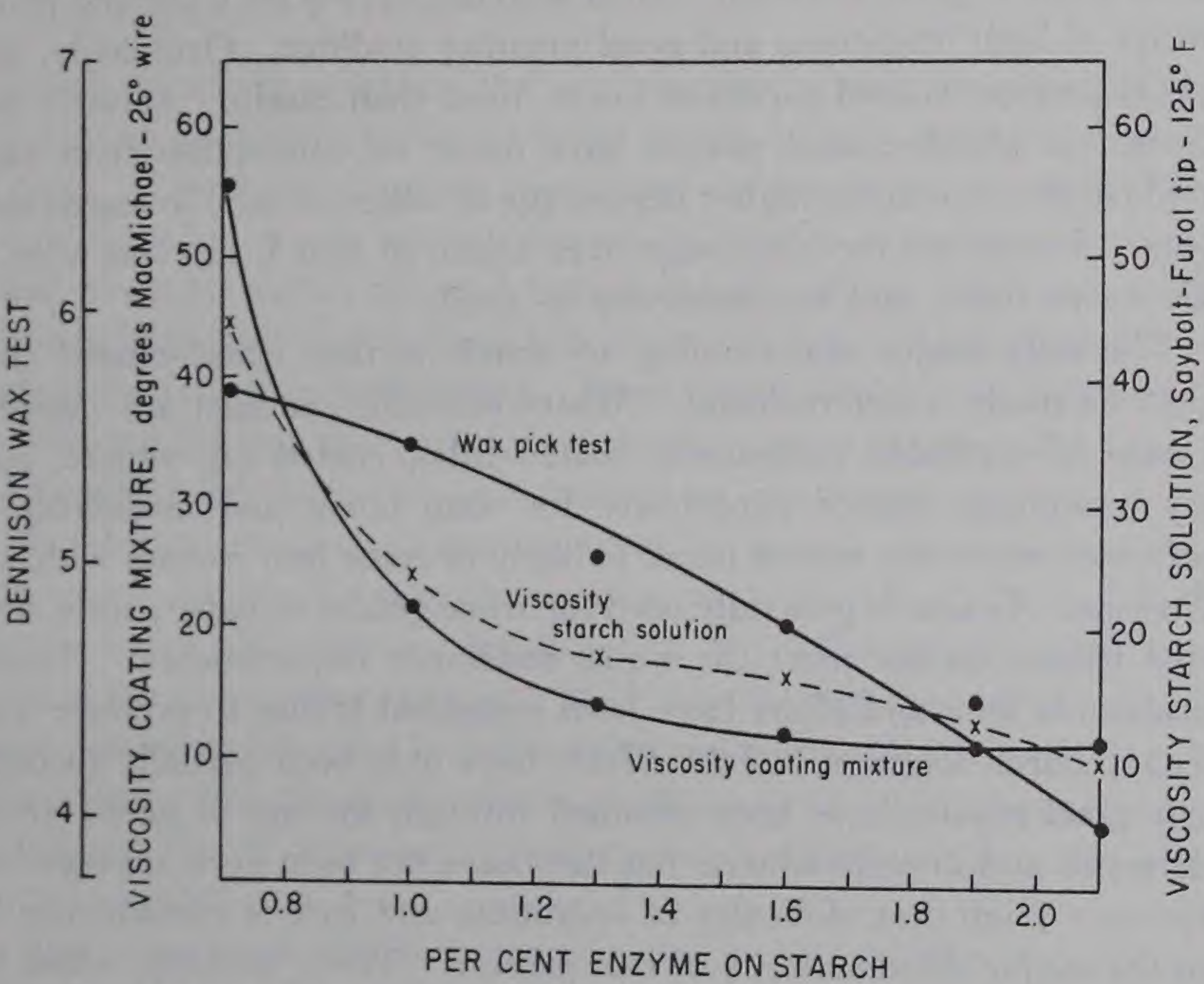

Fig. XVIII-3. Effect of degree of enzyme conversion on the viscosity and pigment bonding strength of starch.

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[19] W. L. Craig, U. S. 2,360,828 (Oct. 24, 1944) and U. S. 2,388,526 (Nov. 6, 1945)

fore the enzyme is added to satisfy the adsorptive demand of the clay particles,[20] or by increasing the amount of agitation during the converting cycle.

In another process for converting starch for high solids coating, the starch is converted with enzyme in the presence of the total amount of water to be used in the coating mixture and dry clay added to the starch after conversion. The clay must be the pulverized, predispersed type, and the coating mixture must be kneaded to bring about a good mixture of starch and clay.

Starch has fair pigment bonding strength (see Fig. XVIII-2), although it is not quite so good as casein. Most starches have good color and produce coatings of high brightness and good printing qualities. Ordinarily, starch tends to produce coated papers of lower finish than casein. Another difference is that starch-coated papers have lower oil absorption than casein-coated papers, due to the higher percentage of adhesive used in starch-coated papers. Starch has the advantage over casein in that it has less odor, less tendency to foam, and less tendency to spoil.

The only major shortcoming of starch is that starch-coated papers cannot be made water-resistant. Water-resistant coatings are desired in the case of washable wallpapers, coated litho, coated tag papers, coated fancy wrappings, coated paperboard for soap boxes and medicinals, and other cases where the coated paper is likely to come into contact with water during use. Casein is generally used for these grades of paper, since starch-coated papers do not meet the water resistance requirements. However, considerable time and effort have been expended trying to produce water-resistant starch coatings, but the efforts have only been partially successful. Fairly good results have been obtained through the use of urea-formaldehyde resins and dimethylolurea, but they have not been good enough for all purposes. High cost, difficulty of operation, and lack of permanence have been the major disadvantages of this process. Three methods which have given fairly good results are described below.

Method 1: Cook 75 parts of oxidized starch, 25 parts of dimethylolurea, and 400 parts of water at 200 to 212° F. for 10 to 15 minutes at a *p*H of about 7.0. Cool the mixture and add to the pigment slurry in the regular manner. Adjust the *p*H of the coating mixture to 5.0 to 5.5 with hydrochloric acid and coat as usual. The use of a dispersing agent such as sodium hexametaphosphate is beneficial in maintaining a high fluidity of the coating mixture at this *p*H level. In order to obtain water resistance by this method, the coated paper must be subjected to high temperature, and even then, the water resistance is only fair.

Method 2: Prepare the coating mixture with cooked starch and pigment in the usual manner. To this, add about 25% of liquid urea-formaldehyde resin on the weight of the starch, and after mixing, add about 10 to 25% of a catalyst (e.g., ammonium chloride) based on the weight of resin. Other catalysts which might be used are ammonium oxalate and diammonium phosphate. Some urea-formaldehyde resins have a tendency to thicken the coating and increase its thixotropic character, whereas others tend to decrease the viscosity of the coating mixture.[21] The addition of the catalyst to the coating mixture always results in an appreciable increase in viscosity. In some cases, best results are obtained by cooking the starch and resin together, instead of adding the resin directly to the coating mixture.

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[20] W. L. Craig, U. S. 2,360,828 (Oct. 24, 1944)

Method 3: This method, which is used mostly in board mills, involves a precoating of the paper with ammonium chloride or alum prior to the application of the starch-resin coating mixture. The alum or ammonium chloride solution at a concentration of about 1 lb. per gallon is applied to the board on the calender stacks, and then the regular starch-clay coating containing about 15 to 25% resin is applied over this precoat. This method gives the highest water resistance of any of the above methods and eliminates the thickening effect obtained when the ammonium chloride is added directly to the coating mixture.

In all the above processes, the coated paper should be subjected to as much heat as possible in order to speed up the reaction between the starch and resin. If possible, the sheet should be heated to approximately 212° F. and held there for twenty to sixty seconds. The *p*H of the base paper is important, since *p*H values above 7 tend to retard curing of the resin. Time is another important factor, since the water resistance tends to increase on aging up to about one week's time. Even under ideal conditions, the coatings obtained are not waterproof, but merely water-resistant; the bond is a wet-strength bond similar to that obtained in wet-strengh papers.

Another method of producing insoluble starch coatings is with antimony salts, specifically potassium pyroantimonate ($K_2H_2Sb_2O_7$).[22] Satisfactory water resistance is obtained with 10% of pyroantimonate on the weight of the starch when used at a *p*H 7.0 to 7.8, but the coated paper containing antimony salt must be heated to a temperature of 220° F. for 30 to 120 seconds. The results are fairly satisfactory if high temperatures can be used, but like all schemes for making starch water-resistant, the process is rather expensive.

The presence of starch in coated papers can be detected qualitatively by the iodine test. The amount of starch can be determined quantitatively by the standard method of starch analysis.[23]

Soy Flour and Soybean Protein

Soy flour and isolated soybean protein are two products derived from soybeans which are used in paper coating. Of the two products, isolated soybean protein is much more suitable for coating; it can generally be substituted for casein on an equal weight basis. Soy flour is used only in small quantities, and then generally as a low-cost extender for casein.

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[21] P. S. Hewett, R. E. Carter and R. J. Church, *Paper Trade J. 124*, No. 24: 263–268 (June 12, 1947)

[22] L. Gussman, N. M. Frisch and M. L. Cushing, *Tappi 33*, No. 7: 328–332 (July, 1950)

[23] See TAPPI Standards

There are two processes for making soy flour, the expeller and the extraction processes. In the expeller process, dehulled soybeans are forced at high temperature (350° F.) and great pressure through expellers which mechanically force out the oil. In the extraction process, dehulled soybeans are first flaked to destroy the cell structure and then extracted with petroleum solvent to remove the oil. After the oil is removed, the oil-free residue is ground into soy flour. The two types of flour (expeller and extracted) differ appreciably in their properties. One difference is in their oil contents, which is about 7% in expeller flour and about 1% in extracted flour. The protein, which is the important constituent of the flour, is more denatured in the case of the expeller flour than in the case of the extracted flour because of the high temperatures and pressures used in the expellers. A comparison of solvent-extracted and expeller soy flours is given in Table II.

TABLE II

COMPARISON OF EXTRACTED AND EXPELLER SOY FLOURS
All percentages given on dry substance basis

Analysis	Extracted soy flour	Expeller soy flour
Moisture, %	6.0–6.5	4.2–4.5
Oil, %	0.7–1.0	6.0–8.0
Protein, %	55.0–56.0	48.0–50.0
Water-soluble protein, %	43.0–45.0	....
Fiber, %	2.5–2.8	2.5–2.6
Carbohydrates, %	32.0	....
Ash, %	6.5	5.0–5.5
*p*H	6.5	6.5

Soy flour is sometimes used as the adhesive in the manufacture of washable wallpaper, and it is sometimes used as an extender for casein in the manufacture of regular coated papers. Soy flour is approximately 50 to 55% usable protein, and 45 to 50% inert material, and hence by itself produces a weak coating. Most of the inert material in soy flour is not dispersible by alkali and hence results in small specks in the coating, but this effect is minimized by grinding the flour as fine as possible, usually so that less than 1% is retained on a 300-mesh screen. Another disadvantage of soy flour is that it produces a coating mixture of high viscosity.

To obtain the maximum adhesive strength, soy flour must be dispersed in strong alkali, e.g., sodium hydroxide; the weaker alkalies used with casein are not satisfactory. In special cases, silicate of soda, borax, or sodium bicarbonate may be used, but they do not bring about maximum dispersion of the flour. Increasing the amount of sodium hydroxide increases the adhesive strength of the flour up to about 7% sodium hydroxide on the weight of the flour. Ordinarily, between 4 to 7% sodium hydroxide on the basis of the dry soy flour is used. The following represents a typical formula: 100 parts soy flour, 400 to 500 parts water, 8 to 14 parts of 50% sodium hydroxide solution. Heating the dispersion to about 130° F. slightly increases the bonding strength and appreciably reduces the viscosity, but prolonged heating should be avoided, since this discolors the flour and tends to reduce the bonding strength. The addition of a small amount of carbon disulfide increases the adhesive strength,[24] but produces a slightly discolored coating. Soy flour dispersions are difficult to keep without spoiling, and for this reason, a preservative should always be included in the formula.

A more desirable adhesive for paper coating than soy flour is isolated soybean protein (trade name, Alpha protein). Soybean protein is made from extracted soybean flakes. The oil-free soybean flakes are treated with a solution of alkali to dissolve the protein, which is then removed by filtration and subsequently precipitated in the form of a curd by adjusting the *p*H of the solution to the isoelectric point of the protein, i.e., *p*H 4.0–4.5. The curd is dried to produce a granulated protein of greater than 95% purity. Almost any alkali can be used for extraction, but some alkalies are better than others. Sodium sulfite is different from other alkalies in that it produces a protein very similar to that in the original soybean. The native soybean protein has a very large molecule and tends to form solutions of high viscosity. It has low adhesive strength when dispersed with weak alkalies, although its adhesive strength is good when dispersed in strong alkalies. If too much alkali is added, the protein gels, but if still greater amounts of alkali are added, the dispersion passes through the gel stage and becomes fluid again. The native protein is also sensitive to heat, tending to gel at temperatures in the neighborhood of 160° F. Because of these disadvantages of native soybean protein, it is customary to modify the protein during manufacture so that it has high adhesive strength when dispersed in weak alkalies and is no longer sensitive to heat.

The manufacture of soybean protein is carried out on a large scale, and consequently the process is readily adapted to large-scale manufacturing methods and controls. One patent[25] describes a method of heat-treating an aqueous suspension of oil-free flakes at a *p*H of 4.5, which coagulates the heat-sensitive proteins and prevents their appearance in the final product. Another patent[26] calls for treating the protein with hydrogen peroxide in a mildly alkaline medium to produce a modified protein which has a lower viscosity than the native protein. Modification is believed to result in a reduction in molecular weight and an unfolding of the globular protein into a linear shape. This gives the soybean protein properties which are very similar to those of casein. Special low-viscosity soybean protein is available commercially.

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[24] I. F. Laucks, U. S. 1,805,773 (May 19, 1931)

[25] P. L. Julian and G. C. Engstrom, U. S. 2,238,329 (Apr. 15, 1941)

[26] R. H. Hieronymous, U. S. 2,274,983 (Mar. 3, 1942)

Commercial soybean protein works very well as a pigment-coating adhesive. It has good pigment bonding strength (see Fig. XVIII-2), being approximately equal to casein in this respect. The color of the bleached protein is good, although the first commercial product was dark in color and produced coatings of low brightness. It is not as readily waterproofed as casein, and has slightly more tendency to foam. In general, however, the coating industry has accepted soybean protein as a satisfactory substitute for casein.

Soybean protein is dispersed with alkali in the same way as casein, but soybean protein is more susceptible to heat than casein, and consequently should not be heated over a temperature of about 130° F. In general, soybean protein produces more fluid coating mixtures than casein, as shown particularly in the range of high adhesive to pigment ratios.

Animal Glue

In addition to casein and soybean protein, there are several other proteins which are used as pigment coating adhesives. One of the most important of these is animal glue. Animal glue was among the first coating adhesives used, but today it is used to a limited extent only, for coated specialty papers, e.g., playing card stock, wallpapers, metal-coated papers, and other grades where a high gloss and a water-resistant coating is desired. Technical gelatin is used in photographic papers.

Either hide or bone glue may be used for coating, but the former gives the best results. In general, the higher the grade, that is, the higher the jelly test, the greater the pigment bonding strength. A medium grade glue has about the same pigment bonding strength as casein. According to Sweatt,[27] animal glues should contain a small amount of grease to keep down foam and help reduce dusting on the calenders, but too much grease is undesirable because of the danger of forming grease spots in the coating.

Glue coatings can be "hardened" or made water-resistant by aftertreatment of the coating with chrome alum or formaldehyde, or with some glues, by mixing about 1 to 3% of alum with the glue solution. The higher grades of glue require less tanning agent than the lower grades to develop the same degree of water resistance.[27] Glue coatings cannot be made as water-resistant as casein coatings.

Corn Proteins

Another class of proteins which are of interest to the paper coating chemist are the corn proteins, which are represented by crude corn gluten or by the purified corn protein known as zein.

[27] H. B. Sweatt, *Paper Ind. 27*, No. 6: 882–884 (Sept., 1945)

Corn gluten, as obtained from the regular corn refining process, is about 60% protein and 40% starch. There is, however, a process for producing a pure destarched gluten. In isolating the gluten, the crude corn gluten is treated with acid at the isoelectric point of the protein in order to solubilize and remove the starch, leaving only the protein. The remaining product is sold as destarched gluten. Corn gluten has never enjoyed a wide usage in the paper industry, principally because of its very dark color and the difficulty of dispersing corn gluten in aqueous media, but some corn gluten has been used as the adhesive in wallpaper coating. The protein is dispersed with ammonium hydroxide and rosin soap, but the color of the solution is quite dark, and the protein must be bleached with peroxide or other bleaching agents for best results.[28] Sulfonated tall oil and sulfonated castor oil have also been used for dispersing corn gluten, but a high percentage of dispersing agent is required. A formula which has been used is: 100 parts corn gluten, 500 parts water, 50 parts sulfonated castor oil or sulfonated tall oil, and 50 parts of 10% sodium hydroxide.

Zein is available commercially in the purified form, and is much superior to the crude gluten for most purposes. Zein is soluble in alcohol and may be dispersed in this medium when used as a protective coating, but alcoholic solutions are not practical for pigment coating. The best dispersing agents for zein in aqueous media are sodium resinate, sulfonated castor oil, and sulfonated tall oil. Chemically modified zein of low viscosity is avaliable commercially. It is dissolved in water to which are added oleic acid, dry rosin size, and an alkali such as sodium hydroxide or ammonia. When ammonia is used, the film is more water-resistant than when sodium hydroxide is used.[29] James[30] found that pigment coatings made from zein are not sufficiently water-resistant for lithographic papers, and recommends[31] the use of a heavy metal salt (e.g., lead acetate) to add water resistance to the coating. Coatings made with zein cannot be tested by the usual wax test, because zein is sufficiently thermoplastic to bond to the hot wax.

Polyvinyl Alcohol

One of the most promising of the synthetic resins for pigment coating is polyvinyl alcohol. Except for its high cost, this material is almost an ideal pigment coating adhesive. It has an exceptionally high pigment bonding strength (see Fig. XVIII-2), and this fact helps to offset the cost disadvantage, since less adhesive is required in the coating formula. For most types of coated papers, 3 to 8 parts of polyvinyl alcohol per 100 parts of pigment are sufficient for good bonding strength.

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[28] J. W. Close, U. S. 2,284,800 (June 2, 1942)
[29] C. R. Keim, *Paper Trade J. 129,* No. 21: 464–465 (Nov. 24, 1949)
[30] A. L. James, *Paper-Maker 104,* No. 4: 148 (Oct., 1942)
[31] A. L. James, *National Lithographer 50,* No. 1: 58 (Jan., 1943)

Polyvinyl alcohol is made in two different grades (see Ch. XI). One grade dissolves fairly readily in cold water, whereas the other must be heated to 70 to 85° C. to effect complete solution. Both types can be obtained in high, low, or medium viscosity. The type requiring heating is the one generally used for pigment coating work. In the process of dissolution, dry polyvinyl alcohol should be added to cold water (20° C. or lower) and stirred until all lumps are broken up and a smooth mixture is obtained. In some cases, this may require considerable stirring. Once the dispersion is smooth, it may be heated with constant stirring at a temperature of 70 to 85° C. until a clear solution is obtained. The solution can then be cooled and added to the pigment in the regular manner.

Polyvinyl alcohol does not produce a water-resistant coating. Water-resistant coatings may be obtained by adding dimethylolurea or urea-formaldehyde resins in a manner similar to that described for starch.[32] In general, polyvinyl alcohol is more easily waterproofed than starch. About 10 to 20% dimethylolurea based on the weight of the alcohol is sufficient to produce a fairly high degree of water resistance where a catalyst (hydrochloric acid or ammonium chloride) is used, and the coated sheet is heated at approximately 200° F. for twenty to sixty seconds. Ammonium chloride should be used cautiously, inasmuch as it has a tendency to thicken the coating. Some people prefer to add the resin and catalyst to the pigment before the adhesive is added.

Cellulose Derivatives

The water-soluble cellulose derivatives, such as methylcellulose, the sodium salt of glycolic acid ether of cellulose (carboxymethylcellulose), and hydroxyethylcellulose, have been used as adhesives in pigment coating.

Methylcellulose has a high bonding strength (see Fig. XVIII-2) and produces highly flexible coatings. It has a high degree of resistance to oil and consequently its use is indicated when a high degree of resistance to ink, varnish, or lacquer is desired.[33] Methylcellulose is soluble in cold water, but is best dissolved by soaking for twenty to thirty minutes in a small amount of boiling water and then adding the remaining amount of cold water (see Ch. XI).

The principal disadvantage of methylcellulose as a coating adhesive is its high viscosity. The product is available commercially in a number of different viscosities, but even the lowest viscosity grade is too viscous for high solids coating mixtures. Water-resistant coatings can be prepared by mixing with urea or melamine-formaldehyde resins in a manner similar to that described for starch.

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[32] Bulletin, "Polyvinyl Alcohol," E. I. du Pont de Nemours & Co., Wilmington, Delaware (1946)

[33] R. M. Upright, M. Kin and F. C. Peterson, *Paper Trade J. 114*, No. 2: 16-20 (Jan. 8, 1942)

Carboxymethylcellulose has been used as a coating adhesive. It has a higher pigment bonding strength than methylcellulose (see Fig. XVIII-2). It is best dissolved by adding to water at 60 to 70° C. with vigorous agitation (see Ch. XI).

Hydroxyethylcellulose is a water-soluble cellulose ether which can be prepared by treating alkali cellulose with ethylene chlorohydrin or with ethylene oxide. The product is fairly soluble in dilute aqueous solutions of alkali up to a relatively high degree of substitution because of the presence of hydroxyls in the substituted group. Alkali-soluble grades of hydroxyethylcellulose have been suggested as pigment coating adhesives in a novel process.[34, 35] In this process, hydroxyethylcellulose is dissolved in dilute sodium hydroxide and mixed with the pigment. Immediately after coating, the wet coating is brought into contact with a dampening roll which applies a solution of a precipitating and neutralizing salt, such as ammonium sulfate. This precipitates the hydroxyethylcellulose from solution by exchanging ammonium ions for sodium ions, thus forming sodium sulfate and ammonium hydroxide. Since the cellulose derivative is not soluble in ammonium hydroxide, it is immediately precipitated from solution. The paper then passes through a set of squeeze rolls which remove the excess salt solution, together with the excess water. The ammonium hydroxide is evaporated during drying of the paper, leaving a substantially neutral coating. When applied in this way, the pigment bonding strength of hydroxyethylcellulose is very good, and the coating has a high degree of water resistance and excellent flexibility. The finished sheet is level and needs no calendering. A suitable formula is:[36]

93 parts clay; 40 parts of water (pH 10.25 with NaOH).
2.5 parts NaOH, 14.5 parts water.
7.0 parts hydroxyethylcellulose, 88.0 parts water, 5.0 parts NaOH.

The final coating mixture contains 5% sodium hydroxide on the total weight of water. There is 7% binder on the basis of the pigment solids, and the total solids content of the coating mixture is 40%.

Synthetic Resin Latices

Synthetic resin latices have been used to an appreciable extent in paper coating. Latices are generally not practical as the only adhesive, but they are useful in blends with other adhesives.

A latex of styrene-butadiene copolymer (sold by the Dow Chemical Company under the trade name of Dow Latex 512-K) has been widely used

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[34] *Paper Mill News 72,* No. 19: 12–14 (May 17, 1949)
[35] D. R. Erickson, *Paper Trade J. 128,* No. 25: 243–244 (June 23, 1949)
[36] D. Robert Erickson, *Tappi 32,* No. 7: 289–291 (July, 1949)

in paper coating since 1946. This material is sold in the form of a milky aqueous dispersion containing 45% solids. It is an anionic latex with a *p*H of 9.0 to 10.5. It is compatible with casein, glue, soy flour, soy protein, and other proteins. Although it is not completely compatible with starch, it works well with starch if it is first stabilized with a small amount of casein, about 3% on the latex solids. Originally, the latex was used only in off-machine coating with casein coating mixtures, but some latex has been used in machine coating. To work satisfactorily in high-speed roll coating, the latex must have a high degree of stability to withstand the high shearing stresses. The latex cannot be used with satin white and certain grades of English clays, but it works very well with domestic clays.

Synthetic resin latex improves the smoothness, gloss, flexibility, and wet rub resistance of the coating. It acts as a permanent plasticizer for other adhesives and improves their flexibility, water resistance, and calendering properties. The wet rub resistance and strength of the coating improve with age, and there is very little loss in flexibility, which is a definite advantage over the results obtained with natural rubber latex.[37] The pigment bonding strength of the latex is high, although it cannot be measured by the wax pick test, due to the thermoplastic nature of the resin. In general, a replacement of 25 to 50% of the regular adhesive with latex will give the desired results.

Blending Adhesives

A number of different adhesives are suitable for paper coating. Because each adhesive has its good points and each has its limitations, attempts have been made to develop suitable blends of two or more adhesives which will combine the good properties of each.

Many attempts have been made to develop a blend of casein and starch which would combine the low cost of starch and the good working qualities of casein. Nearly all these experiments were failures, because protein and starch adhesives are incompatible. It is quite difficult to maintain a uniform mixture of casein and starch, and if conditions are not right, the two will spontaneously precipitate. It is possible to produce a more compatible mixture by using an excess of alkali, but in this case the casein contributes little or nothing toward increasing the water resistance or the bonding strength of the starch, unless it is present in high enough percentage that the adhesive is essentially all casein. The addition of a small amount of casein to a starch coating mixture reduces the bonding strength. Mixtures of soybean protein and starch behave similarly to mixtures of casein and starch.

The mutual incompatibility of starch and casein was used during World War II in the preparation of a special coating for shipping cases used for the packing of synthetic rubber. The rubber, as shipped in those days, was in a very tacky condition and tended to pull fibers from the side of the container. This fiber acted as a serious contaminant, since it interfered with the subsequent processing of the rubber. A small amount of pigment or adhesive in the rubber was not considered harmful, and consequently coated papers were tried, but these, too, were unsatisfactory because the tacky rubber would pull loose not only the coating, but also some of the underlying fiber. It was found, however, that by precoating the paperboard with a starch solution and then applying a clay-casein coating over the dried starch film, a coating was obtained which would rupture between the starch layer and the clay-casein layer and not pull any fiber from the board. The same effect could have been produced by using any two adhesives which had a low degree of compatibility.

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[37] E. K. Stilbert, R. D. Visger and R. H. Lalk, *Tappi 33*, No. 1: 16–22 (Jan., 1950)

There is a modern trend in pigment coating toward double coating, i.e., the use of two or more coatings on the same side of the paper. Different adhesives are sometimes used in the separate coatings, but this poses the problem of finding compatible combinations.

Many combinations of the common adhesives are not truly compatible, but there are a few combinations which have enough merit to warrant their use. Soy flour, for example, is compatible with both casein and soybean protein, and was widely used during World War II as an extender with both these products. It was found that up to 25 to 30% of the total binder could be replaced with finely ground soy flour without reducing the strength of the coating or seriously detracting from its other qualities. Animal glue and casein have also been used together in the manufacture of special grades of coated papers.

Methylcellulose-starch and polyvinyl alcohol-starch have been suggested as possible blends in order to combine the desirable properties of the synthetic resin with the low cost of the starch. The synthetic resins contribute film-forming power, toughness, superior adhesive strength, and flexibility to the coating, and in some cases improve the flowing properties of the coating mixture. Starch is incompatible with methylcellulose, however, and consequently mixtures are not satisfactory, although newer products of improved compatibility with starch have been produced. Blends of carboxymethylcellulose and starch offer some promise because of their better compatibility.

Coating Pigments

The pigment is a highly important component of coated paper. The principal functions of the pigment are to fill in the irregularities of the paper surface, to produce an even and uniformly absorbent surface for printing, and to improve the appearance of the coated sheet. In one sense, the adhesive is only of secondary importance, since its principal function is to bind the particles of pigment to each other and to the paper surface.

A pigment must have certain physical and chemical properties in order to be suitable for paper coating. A good pigment should possess all or most of the following properties: good dispersibility in water, correct particle size distribution, high opacifying power, high brightness, low water absorption, non-abrasive qualities, chemical inertness, compatibility with other ingredients of coating mixture, low adhesive demand, and, if colored, a high tinctorial power and color permanence. Because the qualities of the coated paper depend to a large extent upon the pigment, it is highly important to choose the proper pigment or pigment blend for the coating formula.

Clay accounts for approximately 90% of the pigment used in paper coating, but a large number of other pigments are used in smaller quantities. Many grades of coated paper would be impossible to produce without the use of these other pigments. The principal pigments used in paper coating, aside from clay, are titanium dioxide, precipitated calcium carbonate, water-ground calcium carbonate, calcium sulfate, calcium sulfite, barium sulfate, satin white, and zinc pigments. The properties of these various pigments and the methods of preparing the pigment slurry are discussed in the following sections. An attempt has been made in Table III to list the common coating pigments, together with the outstanding properties of each.

TABLE III

OUTSTANDING PROPERTIES OF COMMON COATING PIGMENTS

1. Medium-grade clay—general body
2. High-grade clay—finish
3. Precipitated calcium carbonate—opacity, brightness, affinity for printing ink
4. Water-ground calcium carbonate—brightness, dull finish
5. Titanium dioxide—opacity, brightness
6. Blanc fixe—weight, chemical purity (photographic papers)
7. Zinc oxide—opacity
8. Satin white—finish, brightness

Clay

Clay is the most important single pigment used in the paper industry. Clays have long been used as filling or loading agents, but within recent years, their use as coating pigments has become of great importance.

In the past, clays varied considerably in their properties, even from the same producer. There is still some variation, but clay manufacturers are seeking new ways of improving the uniformity of their product. The development of machine coating has been responsible for many of the improvements made in the physical properties of clays, since this operation imposes more exacting requirements than were formerly necessary.

Nature of Raw Material. The term "clay" is used in different industries to refer to a variety of minerals which differ widely in chemical and physical properties. In the paper industry, the term "clay" generally refers to a naturally occurring hydrous aluminum silicate, known also by the names of kaolin or china clay. Kaolinite, which has the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, or $Al_4(Si_4O_{10})(OH)_8$ is considered as the parent substance of kaolin, but impurities such as iron oxides, mica, bauxite, calcite, and unchanged feldspar are also present. Other important clays are those belonging to the illite group, in which some of the aluminum has been replaced by iron and magnesium, and the montmorillonite group ($(OH)_4Al_4Si_8O_{20} \cdot XH_2O$), in which part of the aluminum has been replaced by magnesium and ferric oxide.

Small amounts of montmorillonite are used in the paper industry, particularly for deinking, improving the retention of fillers, and eliminating rosin spots in paper. Bentonite (vol clay) is composed of several members of the montmorillonite group; it is formed from the devitrification and partial decomposition of glassy volcanic ash and is found principally in Wyoming. It is a highly colloidal clay. Kaolinite sometimes contains small amounts of montmorillonite, but this is considered as an objectionable contaminant because of its adverse effect on the flow properties of the clay. Much of the fundamental work done on clay has been done on montmorillonite type clays, rather than with kaolinite, although kaolinite clays are much more important from a papermaking standpoint. The reader should be certain of the distinctions between these two types of clay. Kaolinite clays come mostly from England and from the southern part of the United States, particularly Georgia and South Carolina. Domestic clays are now used to a far greater extent than imported clays.

Clays are formed by the reaction of a weak acid (silicic acid) and a weak base (aluminum hydroxide), which are derived from the parent rock as a result of weathering. The silica and alumina groups combine with each other in various proportions to form a clay particle. Almost any ratio of basic to acidic constituents may result. In kaolinite, the ratio of silica to alumina is always close to 2 of SiO_2 to 1 of Al_2O_3, whereas beidellite (member of montmorillonite group) contains approximately three silica to one alumina, and bentonite (also a member of montmorillonite group) contains about six silica to one alumina. Hence, clays have variable chemical and physical composition, depending upon their source. Chemical analysis can be made on clay by dissolving the clay in sulfuric and hydrofluoric acids, or by fusion with alkali. An approximate analysis of Georgia (kaolinite) clay is given in Table IV.[28]

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[28] "Kaolin Clays and Their Industrial Uses," J. M. Huber Corp., New York, N. Y. (1949)

TABLE IV

Chemical Analysis of Typical Georgia Clay

Al_2O_3	39.42
SiO_2	44.32
Fe_2O_3	0.67
TiO_2	1.29
CaO	0.68
MgO	0.21
H_2O (combined)	13.95

Some clays have a lower *p*H than others, that is, they are isoelectric at a lower *p*H than other clays, because of a higher ratio of acidic to basic groups in the clay particle. Thus, beidellite is more acid than kaolinite because it contains a higher proportion of silica. The *p*H of domestic (Georgia) clays is usually between 4.3 to 7.0. The *p*H is generally higher the lower the concentration of the clay suspension, but remains reasonably constant at concentrations over 25%.[39] The acidity of clays, which is determined by titrating a suspension of the clay with 0.1 *N* sodium hydroxide using phenolphthalein as the indicator, is important, since clays having a high acidity cause trouble by thickening protein adhesives, such as casein or soybean protein.

Clays are classified into two types, residual or primary clays, which remain where they were formed, and transported or secondary clays, which are eroded and redeposited in another locality. The Georgia kaolinite clays are sedimentary clays, whereas the English clays are of primary origin. As a rule, the primary clays contain a relatively high percentage of grit, mica, and other foreign materials which must be removed before the clay is suitable for papermaking. On the other hand, secondary clays are relatively free from grit and mica.

The quality of the final clay depends to a considerable extent upon the purity, composition, and uniformity of the clay deposit, which should be as free as possible from grit, mica, and other impurities. Many clay deposits are unsatisfactory because of the presence of impurities. Free silica or quartz is the commonest impurity, and it is often present in the form of large particles, as well as small grains of silt. A frequent and troublesome impurity is iron, which tends to lower the reflectance of clay. The iron content of clay generally varies from 0.15 to 2.0% expressed as ferric oxide on the weight of the clay, and this is mostly chemically bound to the clay. American kaolinite clays usually contain small amounts of titanium dioxide (about 2–4%). Other impurities are calcium, magnesium, manganese, sodium, and potassium.

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[39] "Kaolin Clays and Their Industrial Uses," p. 104, J. M. Huber Corp., New York, N. Y. (1949)

Methods of Processing Clay. Clays are mined by both open-face and underground methods. In the open-face method, the overburden is stripped off and the clays are mined by means of power shovels or scrapers. Clays are processed by (*1*) dry process, or air separation, or (*2*) wet process or classification in water suspension, the latter giving the more complete refining.

If the clay is to be air-separated, it is first precrushed and then finely ground. Air flotation using a whizzer separator removes impurities which are highest in specific gravity, but there is no essential change in the particle size or brightness of the clay. Air-floated clays contain about 1 to 2% moisture and are light and fluffy in appearance, although some air-floated clays are treated with water to form small pellets; they are generally shipped in 50-lb. paper bags or in bulk. Air-floated clays are used for filling of paper, but are not suited for paper coating.

In the wet process, the clay is suspended in water, treated with a dispersing agent, and then is passed through separators or continuous centrifuges where it is classified into fractions of controlled particle size range. The brightness is often improved as much as three points by fractionation. The clay is then flocculated and separated from the water by settling and filtering, and finally by drying. The clay is sometimes bleached with zinc or sodium hydrosulfite to reduce the ferric iron to ferrous iron and produce a whiter product. Bleaching increases the brightness of the clay by 2 to 7 points, making a total possible increase of about 10 points in brightness on refining. Drying of the clay is an important step, since overdrying tends to produce a clay which is hard to redisperse in water. Most of the English clays and many of the high-grade American clays are water-processed. The products are used in paper coating and, to some extent, for filling. Ordinarily, water-processed clays contain from 3 to 8% moisture. The lump type washed clays have a higher density than air-floated clays and are generally sold in 100-lb. paper bags or in bulk. Special pulverized washed clays are produced; these have a lower density and are generally sold in 50-lb. paper bags or in bulk. Water-treated clays have higher brightness, lower screen residue, reduced abrasiveness, and more controlled particle size compared to air-treated clays.

Clay is sometimes sold in slurry form at a solids content of 70%, using insulated tank cars for transporting. Clay in this form is desirable for paper coating, because the physical properties of the clay particle have not been affected by the high temperatures normally used in drying the clay. This results in coatings of higher finish and less tendency toward dusting, and increases the life of the calender rolls used in calendering the coated paper.

Properties of Clay. Clay has a specific gravity of about 2.57 to 2.63. The index of refraction is about 1.56, although clay has been reported to contain another component or components of much higher index of refraction.

Most clays do not exceed a brightness of 85%, and certain clays have a brightness as low as 65%. Recently, however, improvements have been made so that clays are now available up to a brightness of 95%. Most clays are specified as to brightness. In making a brightness test on dry clay, a sample passing a 200-mesh screen is compacted in a metal cylinder under uniform pressure of 30 to 60 p.s.i.[40, 41] A thoroughly cleaned glass plate is placed upon ordinary bathroom scales, and the metal cylinder is placed on top of the plate. About 15 g. of dry clay are added to the cylinder and, with the cylinder held firmly against the plate, a plunger is inserted and forced downward to give the desired pressure on the scales. The plunger is then removed, the cylinder is lifted from the plate, and a brightness reading is made on the smooth, exposed surface of the compacted clay at a wavelength of 457 millimicrons. The moisture content of the clay affects the reading, since there is a progressive loss in brightness as the moisture is increased from 2 to 10%.[41, 42] For this reason, the clay should be carefully dried before testing at temperatures not over 105° C. so that the moisture content is below 1.5%. A study (made by Edgar Brothers Co., McIntyre, Georgia, in 1948) of the testing of clays for brightness in a number of different laboratories has shown that the probability of missing the true brightness at the 10% probability-level is 1.12 points, and at the 5% level, is 2.25 points, if the clay is not pulverized before testing. If a pulverizer is used, the values are reduced to 0.80 point at the 10% probability level and 1.61 points at the 5% probability level. It is recommended that brightness tests be made in triplicate to obtain worth while precision.

If the moisture content is too high, clay does not flow properly and becomes difficult to handle. If it is too dry, clay dusts badly. The moisture content should be taken into account in calculating the solids content of high solids coatings. The moisture content of clay may be determined by (*1*) toluene distillation, (*2*) by electronic measurements based on the relationship between moisture content and electrical capacity, (*3*) by mixing a definite weight of clay in a definite weight of distilled water, together with a small amount of pyrophosphate and determining the specific gravity with a sensitive hydrometer, or (*4*) by oven drying at 100 to 105° C. Because clay tends to lose moisture slowly, it is desirable to heat samples for at least ten hours. Clay loses water above its normal moisture content when heated at temperatures over 105° C. The amount of water loss de-

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[40] I. L. Lester and S. C. Lyons, *Paper Trade J. 125*, No. 17: 189–195 (Oct. 23, 1947)

[41] N. Millman, *Paper Trade J. 127*, No. 13: 43–45 (Sept. 23, 1948)

[42] "Kaolin Clays and Their Industrial Uses," p. 97, J. M. Huber Corp., New York, N. Y. (1949)

pends upon the type of clay and the temperature as shown in Figure XVIII-4.[43]

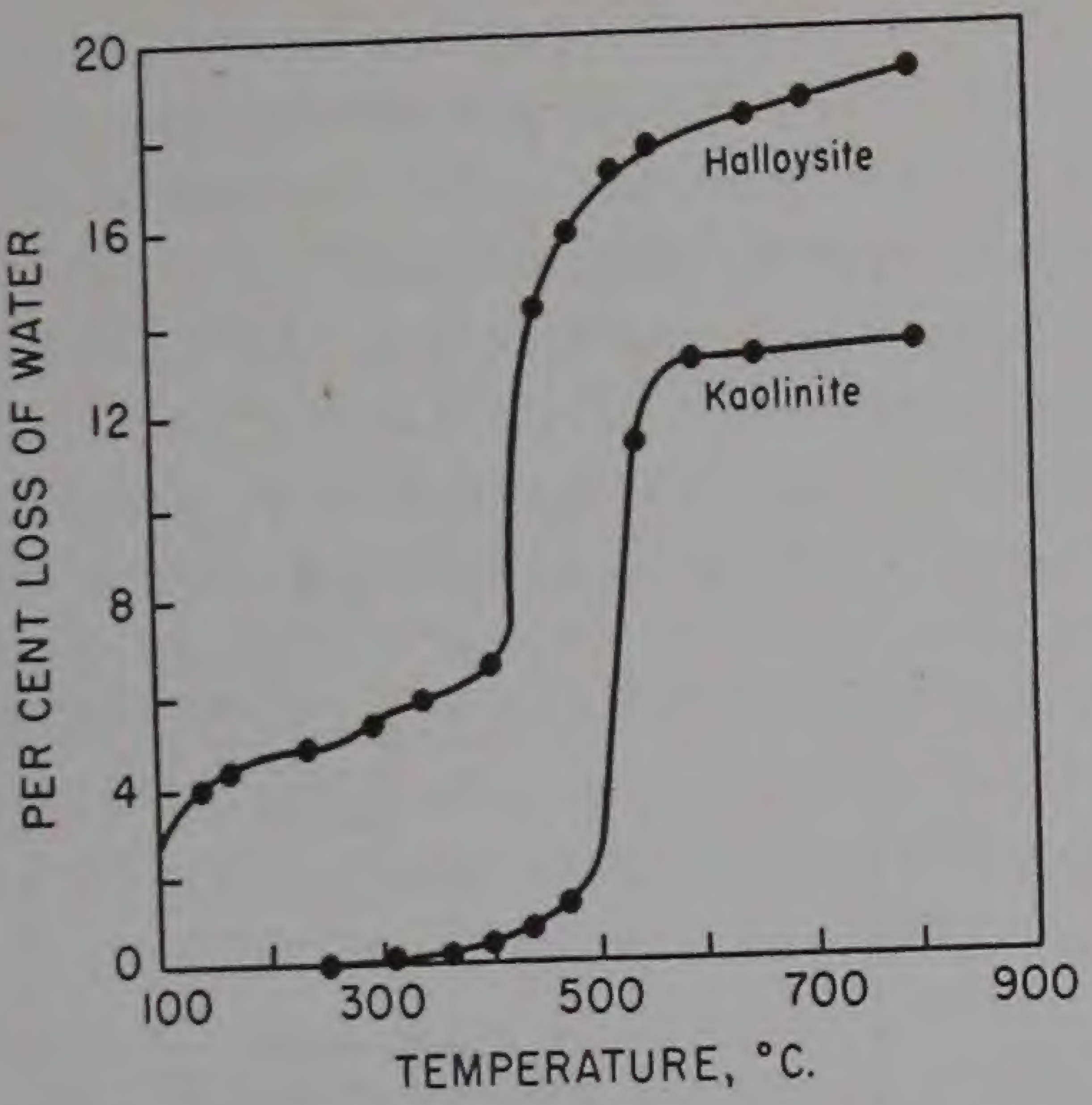

Fig. XVIII-4. Effect of heat on water loss of kaolinite and halloysite.

Ion Exchange Properties of Clay. The free acidic and basic residues on the surface of the clay particle are free to dissociate into ions or to react with ions in the surrounding medium. In the natural state, varying amounts of ions, such as Ca^{++}, Mg^{++}, K^{+}, and Na^{+}, are adsorbed on the surface of the clay particle. Surrounding the clay particle is a micellar atmosphere containing adsorbed and unadsorbed ions which bring the clay particle into equilibrium with the surrounding medium. This forms a diffuse double layer about the clay particle, as shown in Figure XVIII-5. This layer has

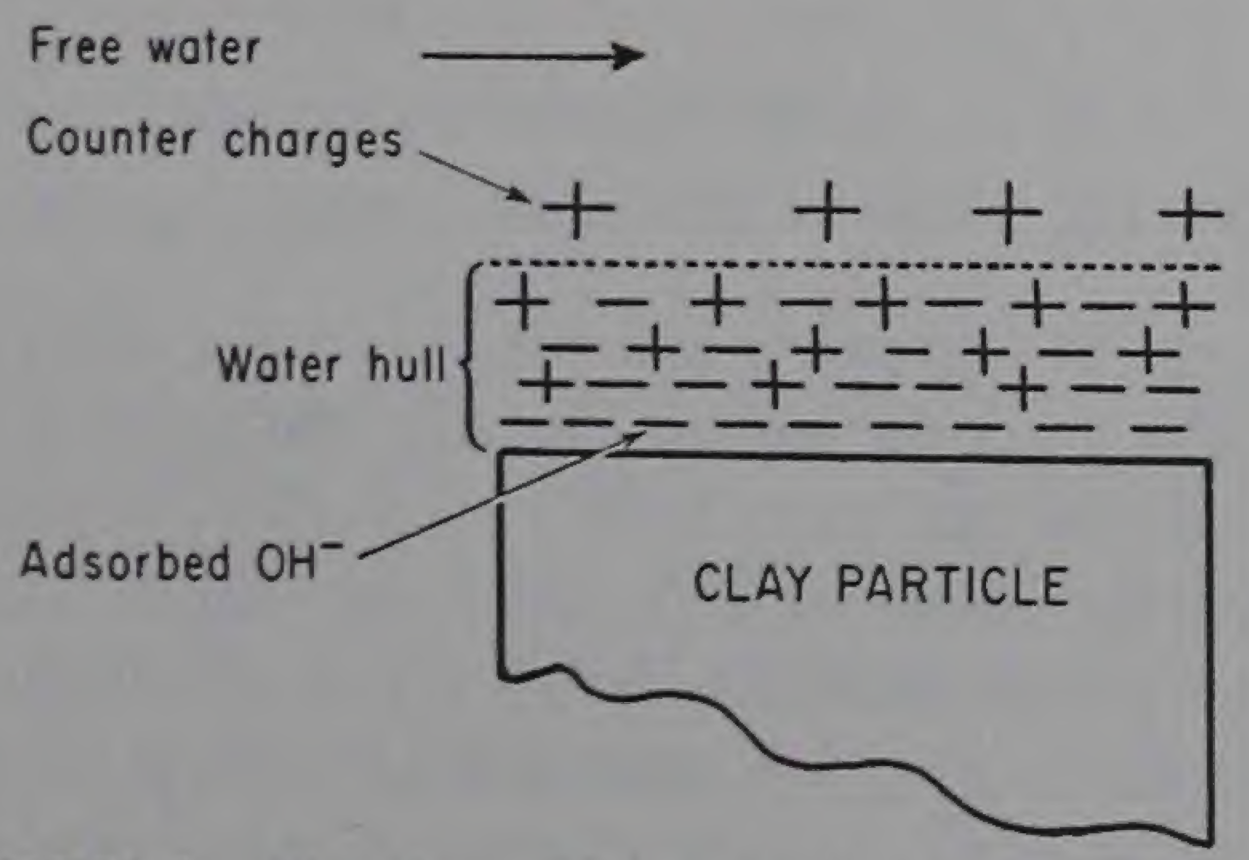

Fig. XVIII-5. Showing diffuse double layer surrounding clay particle (courtesy Edgar Bros. Clay Co.).

an important effect upon the hydrating properties and flow characteristics of the clay.

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[43] C. S. Ross and P. F. Kerr, U. S. Government Printing Office, Paper 185–6, 1934, p. 140

The colloidal properties of clay are due to the colloidally active surface layer surrounding the more or less stable core. Thus, the colloidal properties of the clay depend as much upon the activity of the clay surface as upon the particle size. It is conceivable that a clay with a large particle size might exhibit greater colloidal properties than a smaller particle size clay, due to the greater activity of its surface.[44]

The firmness with which adsorbed ions are held by clay follows the following decreasing order: Al^{+++}, Fe^{+++}, H^+, Ca^{++}, K^+, and Na^+ for cations, and OH^-, PO_4^{---}, SO_4^{--}, and Cl^- for anions.[45] By nature, clay adsorbs hydroxyl groups more strongly than hydrogen atoms; hydroxyl ions are not displaced except at extremely low *p*H. If a salt such as NaCl is added to a clay suspension, both the sodium ion and the chloride ion are adsorbed with equal firmness (at the correct *p*H); if $NaSO_4$ is added, however, the sulfate ion is adsorbed more strongly than the sodium ion.

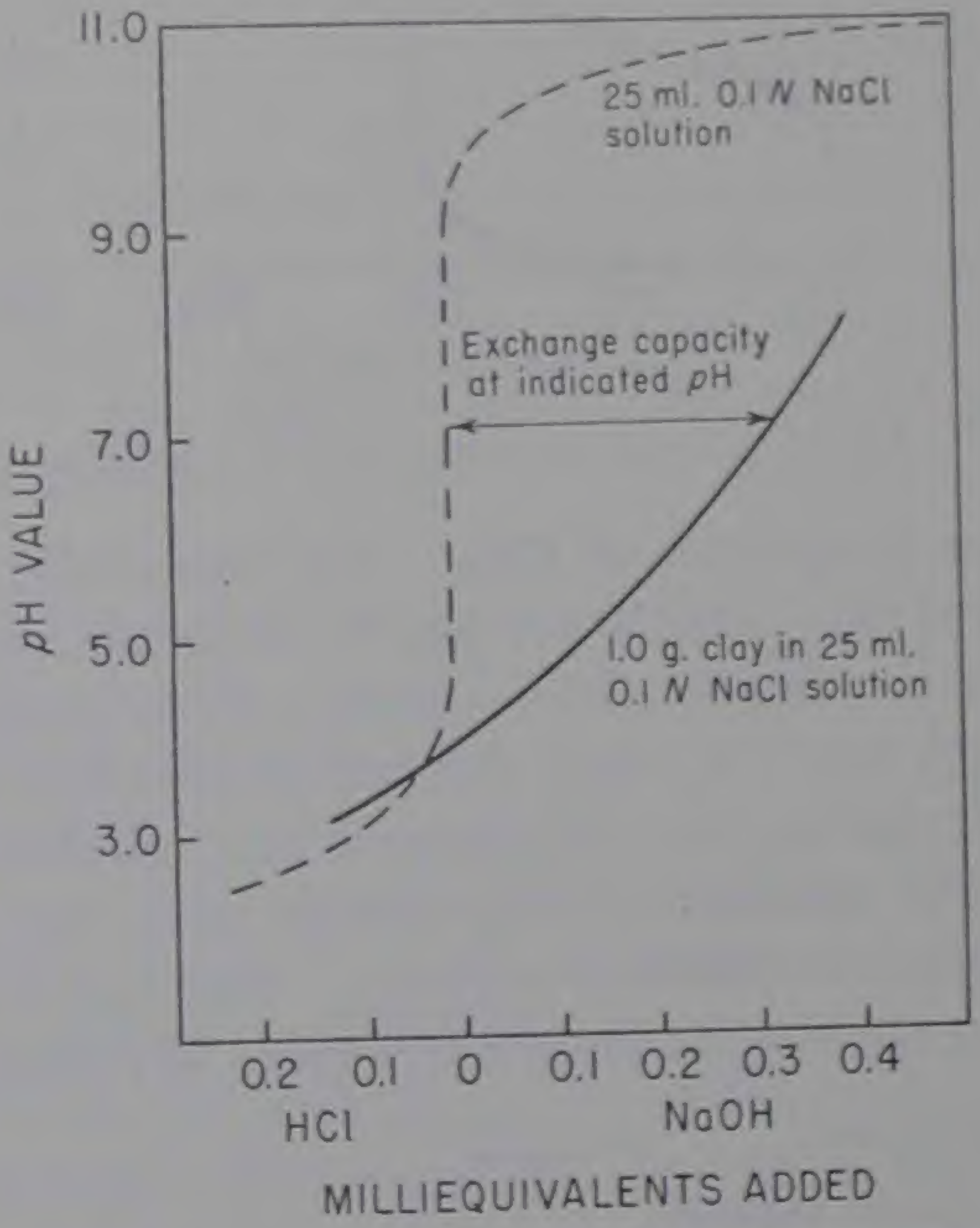

Fig. XVIII-6. Effect of *pH* on the exchange capacity of clay.

The *p*H of exchange neutrality is the *p*H at which the clay particle adsorbs an equal number of cations and anions from a neutral salt. Below this *p*H, an excess of anions is adsorbed, and above this *p*H, an excess of cations is adsorbed. The *p*H of exchange neutrality for ordinary china clay occurs at a *p*H less than *p*H 3, which means that the anion exchange properties of clay are of little practical importance. The *p*H of exchange neutrality and the exchange capacity of an electrodialyzed clay in equilibrium with sodium chloride is shown in Figure XVIII-6, which was taken from work by Meyer.[46]

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[44] W. W. Meyer, *J. Research Natl. Bur. Standards 13*, No. 2: 245–258 (Aug., 1934)

[45] C. G. Albert, *Trans. Electrochem. Soc. 73:* 173–182 (1938)

The composition of clay, i.e., the ratio of acidic to basic residues, determines the ion exchange characteristics. A clay with a high percentage of acidic residue tends to have a high exchange capacity for cations. In general, the exchange capacity varies from 15 to 100 milliequivalents of exchangeable cations per 100 g. of clay.[47] This depends upon the type of clay, as shown in Table V, which gives the base exchange capacity of a number of clays as reported by Grim.[48] Hauser[47] points out that bentonite undergoes base exchange in the interior of the particle and hence is not affected by fineness of the particle. In comparison, the base exchange of kaolin clays, which have a dense structure, depends mainly on the amount of external surface. Thus, the base exchange properties of kaolinite would be expected to increase with fine grinding.

TABLE V

Base Exchange Capacity of Different Clays

Clay	Milliequivalents per 100 g.
Montmorillonite	60–100
Illite	20–40
Kaolinite	3–15

The higher the ratio of acidic to basic residues in the clay, the lower the isoelectric *p*H of the clay, which means that more hydrogen ions will be required in solution to suppress the ionization of the hydrogen atoms on the surface of the particle.

Hydration of Clay. Water is held by clay in three ways: (*1*) water of combination held in the form of hydrous oxides; (*2*) water of hydration held on the surfaces of the clay particle by molecular attractions; (*3*) capillary, or free, water held in the fine capillaries of the clay particle by surface tension. Kaolinite contains two molecules of chemically combined water, or about 13.96%, whereas halloysite seemingly has four molecules, even though they both have the same ratio of alumina to silica.

The amount of water of hydration increases as the particle size decreases, since this increases the specific surface. The thickness of the water layer about the clay particle is dependent upon the base exchange capacity of the clay and the number and type of adsorbed ions.[49] The clays which are most active in base exchange exhibit the greatest hydrating characteristics. Thus, kaolinite has low hydrating properties because of its low base exchange, whereas illite and montmorillonite are more hydrous than kaolinite because of their greater base exchange capacity.[50] Rowland[51] considers the hydration capacity of the clay as one of its most important properties, because it affects the water-holding capacity and also the flow characteristics of the coating mixture.

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[46] W. W. Meyer, *J. Research Natl. Bur. Standards 13,* No. 2: 245–258 (Aug., 1934)

[47] E. A. Hauser, *Paper Trade J. 105,* No. 7: 111–113 (Aug. 12, 1937)

[48] R. E. Grim, "Modern Concepts of Clay Materials," p. 245, Report No. 80. Dept. of Registration and Education, Urbana, Illinois (1942)

Meyer[52] has shown that substitution of an ion lower in the Hofmeister series (e.g., calcium) for one higher (e.g., sodium) reduces the amount of imbibed water. In other words, calcium ion has a lower hydration capacity than sodium ion, and consequently the substitution of calcium for sodium reduces the hydrous nature of the clay. According to Meyer, certain clays may imbibe a layer of water up to 23 to 45 millimicrons in thickness when treated with sodium.

The crystal sheets in a highly hydrated clay are held together less firmly than those in a slightly hydrated clay. Consequently, even weak shearing forces may cause the crystal planes in a highly hydrated clay to slide over one another and result in a subdivision of the clay particle. This may occur very readily with montmorillonite clays, but is probably not realized in the case of the less cleavable kaolinite clays. According to Grim,[53] the ease of subdivision of a hydrated clay is due to the thin films of oriented water molecules which adhere to the surface of the crystals and act as a lubricating film.

Clays lose their hygroscopic moisture at 100° C., and lose their chemically combined water at about 500° C. The effect of heating on halloysite and kaolin is shown in Figure XVIII-4. Heating clay at very high temperatures is believed to bring about an irreversible dehydration and aggregation of the clay particles,[54] resulting in less freedom of movement for the crystal layers. Such calcined clay has much lower hydrating properties than the original clay. This anhydrous type of clay has interesting possibilities for paper coating because of its high brightness (90–92) and low gloss characteristics, but unfortunately it is extremely abrasive, and coatings containing it are marked easily on contact with metal, and they wear printing plates at an excessively high rate.

[49] W. W. Meyer, *J. Research Natl. Bur. Standards 13*, No. 2: 245–258 (Aug., 1934)

[50] G. H. Sheets, *Paper Trade J. 116*, No. 3: 22–30 (Jan. 21, 1943)

[51] B. W. Rowland, *Paper Trade J. 112*, No. 26: 311–313 (June 26, 1941)

[52] W. W. Meyer, *J. Research Natl. Bur. Standards 13*, No. 2: 245–258 (Aug. 1934)

[53] R. E. Grim, *J. Am. Ceram. Soc. 22*, No. 5: 141–156 (May, 1939)

[54] B. W. Rowland and H. J. Allison, Jr., *Paper Trade J. 111*, No. 3: 25–28 (July 18, 1940)

Shape of Clay Particles. Alumina and silica are combined in clay to form a crystal which is monoclinic. The individual layers are arranged in the form of hexagonal plates. Rowland and Allison[54] visualize a clay particle as similar to a pack of cards where the individual cards are, under certain conditions, free to slide over one another. Nearly all elementary papermaking clays are thin-plated,[55] although Marshall[56] believes that clay particles below 500 millimicrons are not so markedly plate-shaped as the larger particles. An electronmicrograph of the finer particles in kaolinite is shown in Figure XVIII-7, where the typical hexagonal shape is quite apparent. Figure XVIII-8 is an electronmicrograph of an English clay. The

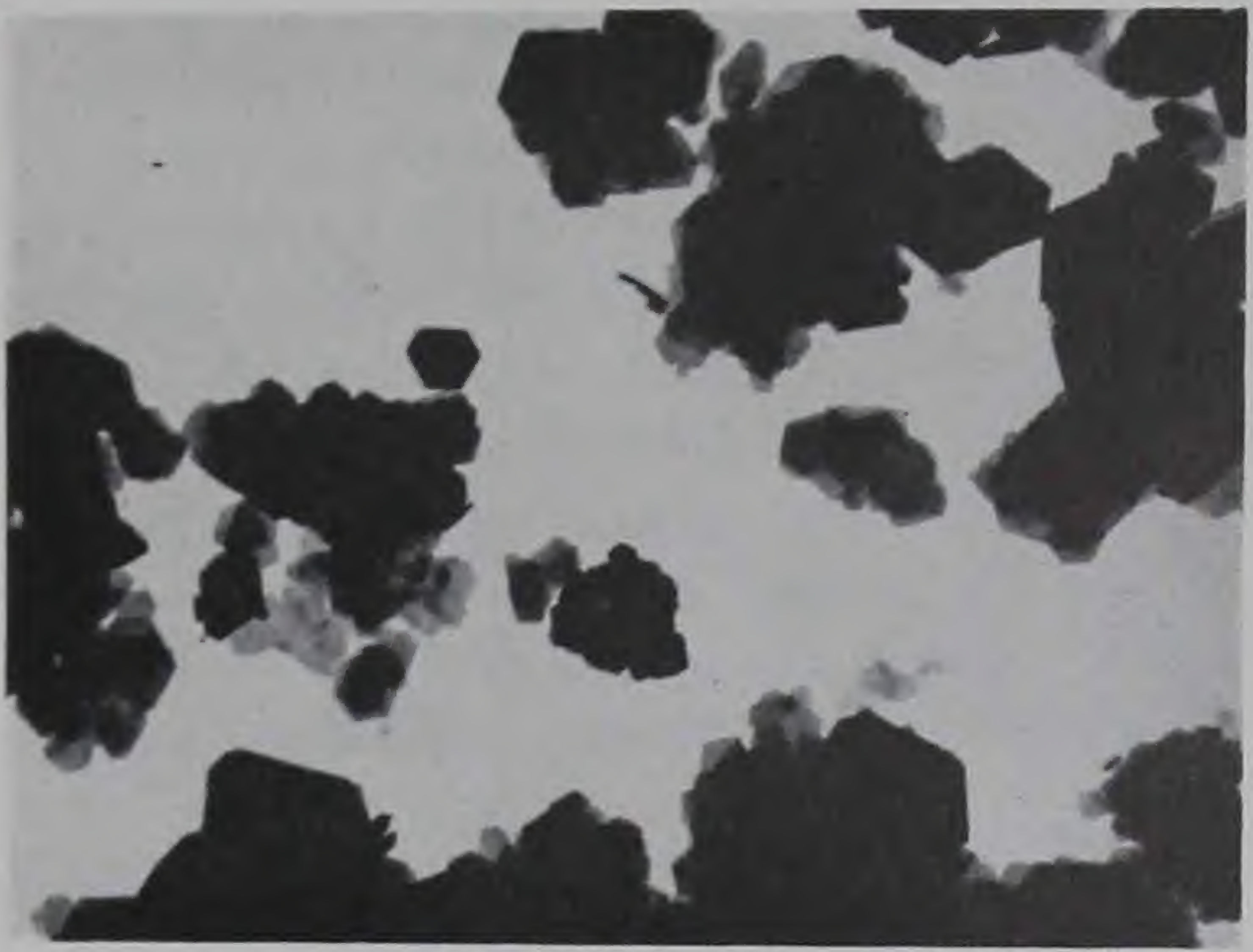

Fig. XVIII-7. Kaolinite clay (10,000×) (courtesy Institute of Paper Chemistry).

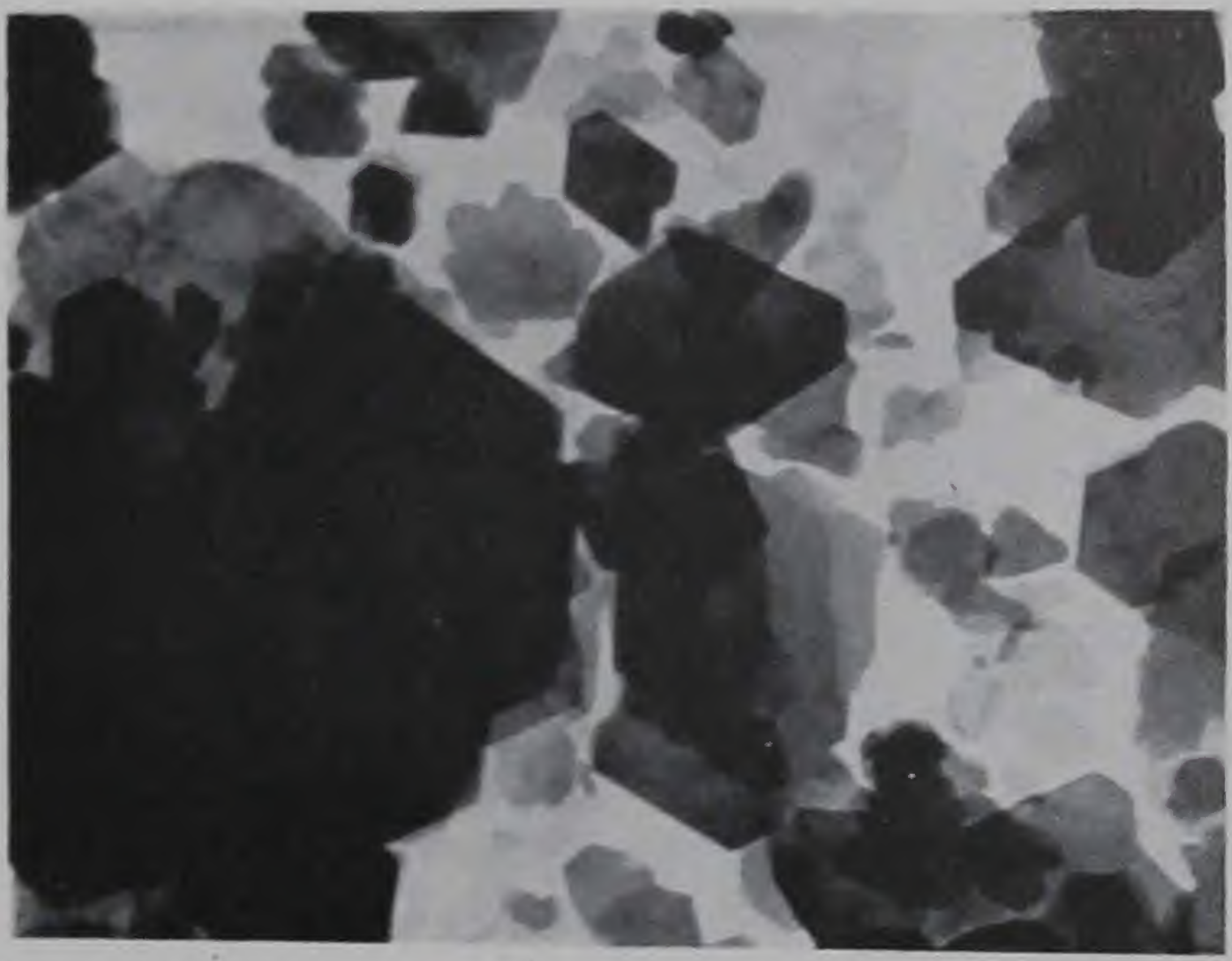

Fig. XVIII-8. English clay (11,500×) (courtesy Institute of Paper Chemistry).

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[55] G. R. Sears and E. A. Kregel, *Paper Trade J. 114,* No. 12: 139–145 (Mar. 19, 1942)

[56] C. E. Marshall, *J. Soc. Chem. Ind. 50:* 444–450; 457–462 (Dec. 4, 1931)

gloss-producing qualities of clays result primarily from their plate-like structure.

Particle Size of Clay. The particle size is an important property of clays, since it determines the opacity, the brightness, the ink receptivity, the adhesive demand, and the flow properties. Particle size has become of increasing importance in recent years. Originally, screen or sieve tests were used for measuring particle size, but this method no longer gives enough information because of the large size of the openings in the screens (325-mesh screen having openings equal to 44 microns, 100-mesh screen having openings equal to 149 microns, etc.). Screening through a 325-mesh screen has been widely used in the past to determine the amount of grit, mica, or trash in clay, and this test is still used somewhat with inferior clays, which contain a considerable amount of mica. An acceptable clay should contain less than 0.02% foreign matter on a 200-mesh screen. However, screen analysis is no longer an adequate criterion of the quality of papermaking clays, and newer methods of particle size analysis have been developed.

Sedimentation methods constitute the most practical means of measuring particle size. Sedimentation curves can be made by plotting the weight of pigment settled out against the time of settling. High-speed centrifuges may be used to speed up the settling. The radius of the particles can then be calculated according to the well-known Stokes equation, which expresses the relationship between rate of settling and particle size. This method is quite accurate down to a particle size of about 1 micron. In making sedimentation studies on clay, the clay is first deflocculated and then centrifuged at low solids. The sediment is collected in calibrated glass tubes and the volume read at selected time intervals. Another method of determining particle size is by taking readings on a clay suspension at regular intervals with the Bouyoucas hydrometer, a specially designed hydrometer which is calibrated to read the grams of material in suspension.[57]

It should be pointed out that particle size comparisons in absolute units means very little unless all measurements are made on a comparable basis. Thus, the reader should use discretion in comparing data on particle size reported for clays or other pigments unless he is certain that comparable methods of analysis have been used. The values of particle size obtained from sedimentation methods are not absolute values, but are, instead, empirical values which are commonly accepted in the industry.

All pigment dispersions are poly-dispersed, and particle size distribution is often a more important factor than average particle size. Either size distribution curves (e.g., curves based on microscopic methods) or weight distribution curves (e.g., curves based on sedimentation methods) can be used. The former method stresses the fine particles in the mixture, whereas the latter method stresses the coarse particles. In general, a pigment which has most of the particles in the optimum range will have greater hiding power, reduced light absorption, and greater over-all reflection than a pigment containing some large and some small particles.[58, 59]

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[57] "Kaolin Clays and Their Industrial Uses," pp. 99–100, J. M. Huber Corp., New York, N. Y. (1949)

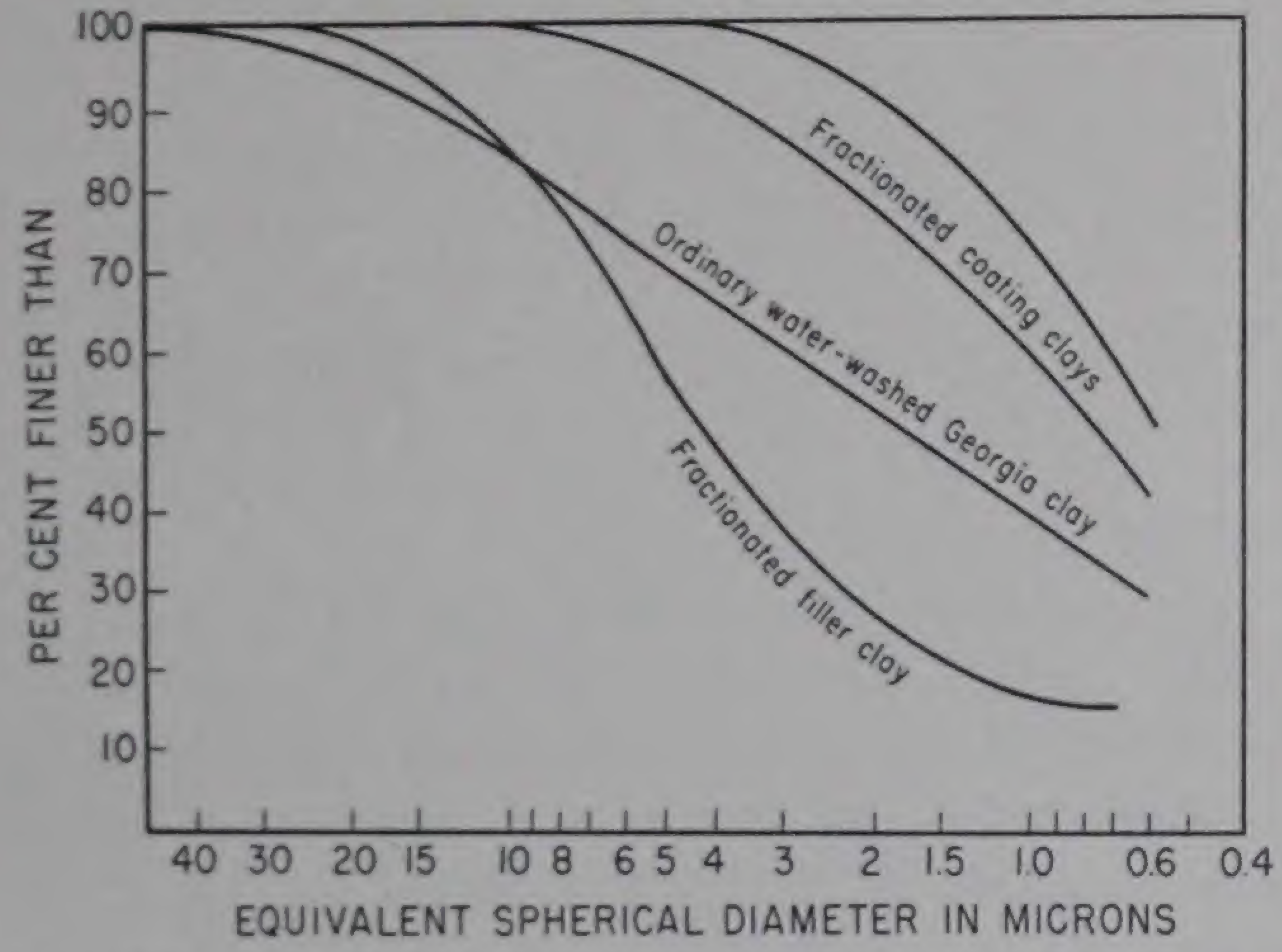

Fig. XVIII-9. Particle size range of several commercial papermaking clays (courtesy Edgar Bros. Clay Co.).

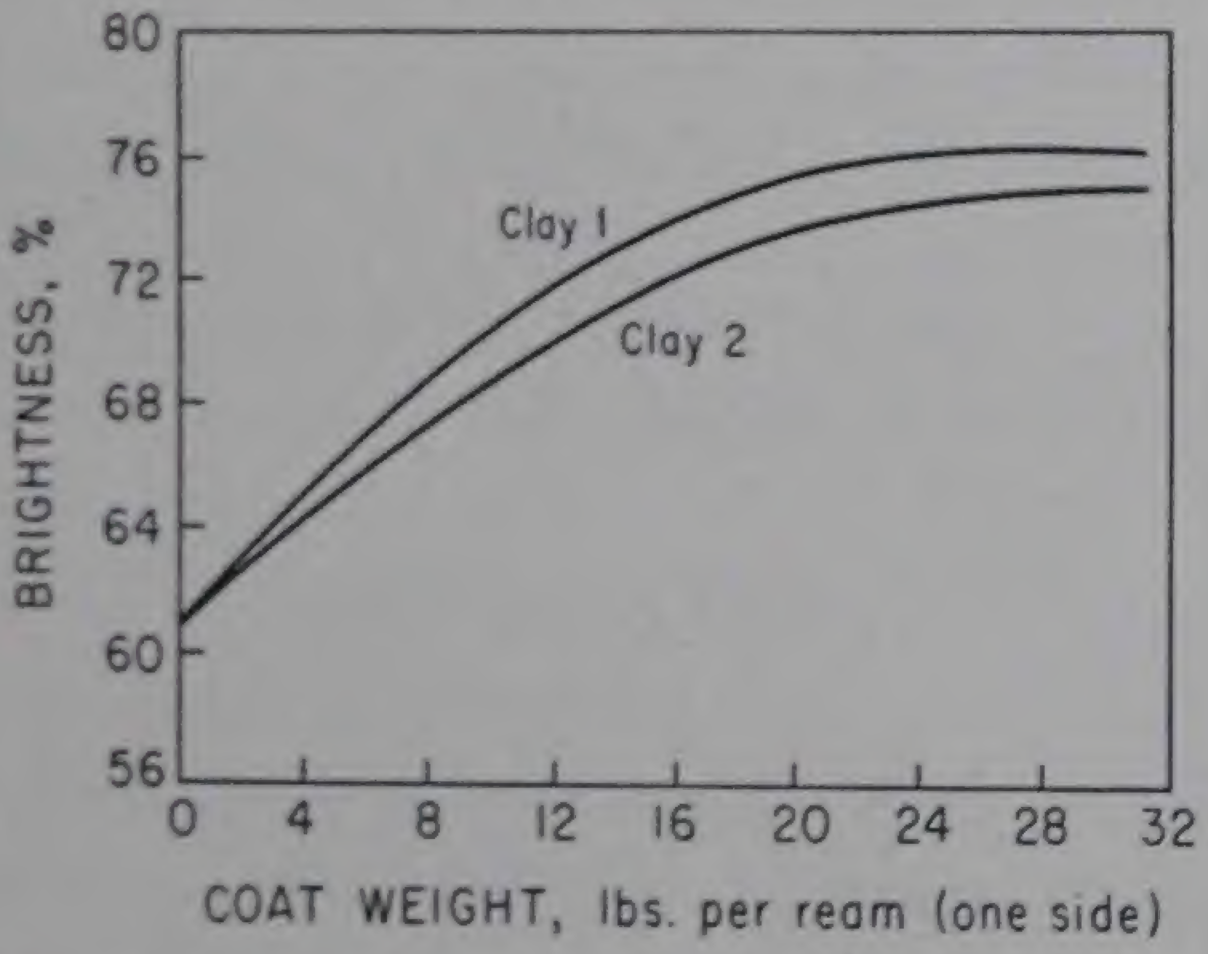

Fig. XVIII-10. Effect of particle size on the covering power of clay (brightness vs. coat weight.)[63] Brightness of raw stock 60%, of clays 85%.

Commercial kaolinite clays do not contain much material in the range commonly accepted as colloidal.[60] Marshall[61] states that English china clays contain practically no particles less than 0.1 micron in diameter.

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[58] D. F. Wilcock, *Ind. Eng. Chem. 33,* No. 7: 938–940 (July, 1941)
[59] L. T. Work and I. H. Odell, *Ind. Eng. Chem. 25,* No. 5: 543–549 (May, 1933)
[60] C. G. Albert, *Trans. Electrochem. Soc. 73:* 173–182 (1938)
[61] Marshall, *Ceram. Soc. Trans. 30:* 81 (1931)

Sometimes clays are graded for convenience into coarse, intermediate, and fine, depending upon the range in which the majority of the particles fall.[62] The range is usually as follows:

Grade clay	Majority of particles
Coarse	Over 10 microns
Intermediate	Between 2 and 10 microns
Fine	Less than 2 microns

Filler clays contain some relatively coarse particles (about 40 to 70 microns in diameter). Coating clays generally range from about 30 microns as an upper limit to about 0.1 micron in size, 70 to 90% of the particles being smaller than 2 microns. Machine coating clays are graded for particle size and generally contain a greater proportion of smaller particles, the range being from 8 to about 0.1 micron. Particle size distribution curves for several different commercial clays are shown in Figure XVIII-9. Regular coating clays generally contain 70% finer than 2 microns and machine coating clays usually contain 80% finer than 2 microns.

The proper size for coating clays depends on the results to be obtained. The thickness of the dried coating on the average coated book paper (15-lb. coating) is in the neighborhood of 12 to 15 microns, so that obviously no pigment particle should be greater than this in diameter. On the other hand, pigments which are too small would increase the adhesive demand beyond all reason. It would appear that a pigment composition containing particles the majority of which are between 0.4 and 3.0 microns in diameter has the most desirable composition from a coating standpoint. To some extent, the optimum particle size depends upon the weight of coating applied.

Particle size has a very definite effect on the covering power, brightness, and gloss of clay-coated papers. The effect of particle size of clay on covering power as measured by the brightness of the coated paper is shown in Figure XVIII-10 for two grades of coating clay having the following particle size distribution.[63]

Diameter, microns	Clay 1, %	Clay 2, %
Above 10	0.0	1.0
5–10	3.3	6.6
4–5	2.8	4.2
3–4	4.8	6.8
2–3	8.6	9.4
1–2	15.4	15.3
0.5–1	17.2	16.0
0–0.5	47.9	40.7
Finer than 2	80.5	72.0

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[62] S. C. Lyons, *Paper Trade J. 106*, No. 26: 384–385 (June 30, 1938)

[63] "Kaolin Clays and Their Industrial Uses," J. M. Huber Corp., New York, N. Y. (1949)

It can be seen from Figure XVIII-10 that the finer clay has the higher brightness. This is due partly to the natural higher brightness of the finer clay and partly to the greater number of air interfaces arising from the greater surface area. Fine clays produce coatings of higher gloss than coarse clays, clays of particle size less than 2 microns producing the maximum gloss. For the two clays used in the above example, clay No. 1 (the finer clay) produced a gloss of 39 compared to a gloss of 37.5 for clay No. 2.[63] However, fine clays do not stand calendering as well as coarse clays and are more likely to produce blackening on calendering.[64] Where gloss is of primary importance, it is undesirable to have more than 5% of the particles over 2 microns.

Dispersing Clay in Water. In order to prepare a satisfactory coating mixture, it is necessary to reduce the clay to the proper state of subdivision. Most clays are received at the coating mill in the dry form, and they must first be mixed with water and then agitated. Good working or flow properties of the coating mixture are dependent upon the proper dispersion of the clay. The properties of the final coated sheet are also enhanced by dispersing the pigment as completely as possible. Many coating mills use "dough" mixers, mechanical dispersing equipment such as ink mills, pebble mills, or colloid mills, but these are generally used on the coating mixture after the adhesive is added and not on the pigment dispersion.

Clays as received commercially are not dispersed into their ultimate particle size, since the unit particles are held together firmly in the form of aggregates. Even violent agitation will not break the aggregates down permanently, unless a dispersing agent is used. However, a clay (kaolin) suspension containing particles all of which were larger than 3 microns was found to have all the particles reduced to a size less than 3 microns after milling with sodium silicate.[65]

Dispersing agents are essential in preparing free-flowing clay suspensions at high solids content. The best dispersing agents are sodium silicate, sodium pyrophosphate, sodium hexametaphosphate, specially purified sodium lignosulfonate, and alkaline casein. Some of the ordinary alkalies, such as trisodium phosphate, sodium hydroxide, and sodium carbonate, are effective, but not so effective as the above. Silicates of high silica content make better dispersing agents than the more alkaline grades, silicate of the ratio $Na_2O \cdot 4SiO_2$ being best. The most effective dispersing agents (e.g., sodium silicate, sodium hexametaphosphate, and sodium pyrophosphate) produce highly fluid suspensions at 75 to 80% solids using only 0.2 to 0.5%

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[64] S. C. Lyons, *Paper Trade J. 106,* No. 26: 384–385 (June 30, 1938)

[65] R. D. McCarron and B. W. Rowland, *Paper Trade J. 96,* No. 22: 36–39 (June 1, 1933)

dispersing agent on the weight of the clay. Figure XVIII-11 shows the relative efficiencies of several different dispersing agents. Tetrasodium pyrophosphate is used quite extensively for clay deflocculation. It is not so efficient as sodium hexametaphosphate, but it is cheaper. Another material that has found some favor for clay deflocculation is sodium tetraphosphate ($Na_6P_4O_{13}$).

Some clays are difficult to mix into water without balling up. The best procedure is to add the water and a dispersing agent to the mixer first, followed by the clay. Another method is to add part of the water, followed by part of the clay, and then gradually to add more clay and water at intervals. It is desirable that the clay suspension have sufficient viscosity while it is being dispersed in order to offer resistance to the mixing blades. If too much water is present, there will be insufficient rubbing and shearing action between the clay particles to produce the desired breakdown in particle size. Of all the pigments used in paper coating, clay is probably changed more than any other by the work done upon it. Arnold[66] found that the greatest changes in milling take place in clay suspensions containing the lowest percentage of dispersing agent. Milling tends to increase the viscosity of the slurry unless enough dispersing agent is present to satisfy all the newly exposed pigment surface which is created during milling.

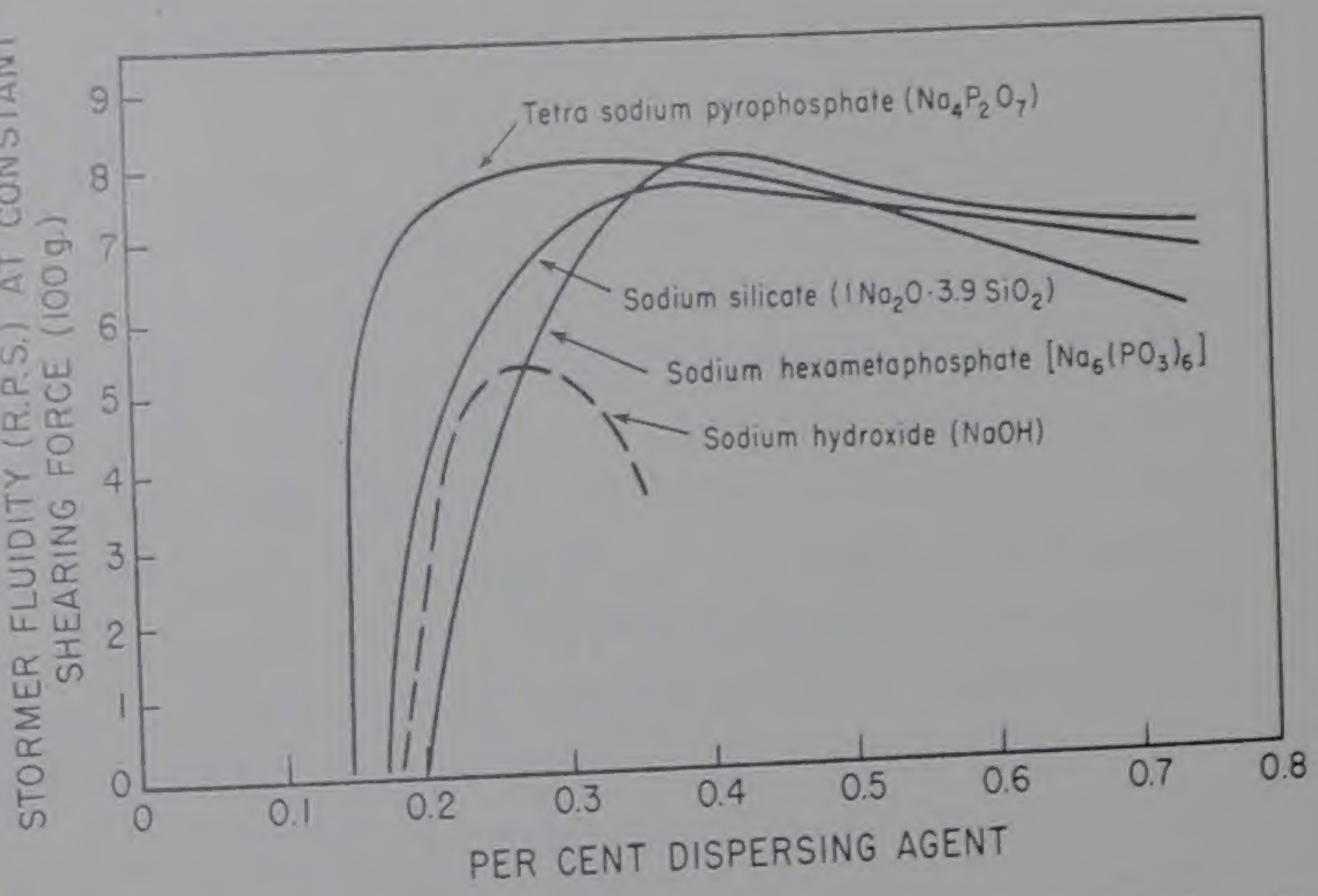

Fig. XVIII-11. Effect of different dispersing agents on the viscosity of clay-water suspensions (courtesy Edgar Bros. Clay Co.).

It makes a difference whether the dispersing agent is added to the water before or after the clay, or whether it is added before or after milling. In general, best results are obtained by adding the dispersing agent to the water before the clay. The amount of dispersing agent used should be based on the weight of the clay rather than on the amount of water present. The amount of water in the mixture has some effect, however, since Arnold[66] found that the amount of dispersing agent required for minimum viscosity increases as the amount of water in the slurry is decreased. The correct amount of dispersing agent should be carefully determined and then rigidly adhered to thereafter in order to maintain a uniform coating mixture. If too much dispersing agent is used, a rethickening or a flocculation of the clay may result, particularly when using sodium silicate, which is sometimes quite critical in its effect on the viscosity. If less than the required amount of dispersing agent for minimum viscosity is added, the clay suspension may show an intense thixotropic build-up.[67]

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[66] K. A. Arnold, *Paper Trade J. 117*, No. 9: 98–104 (Aug. 26, 1943)

The mechanism of dispersing agents is not well understood, although it is generally believed that they increase the acid character of the clay particle surface, thereby creating more surface activity. The negatively charged ions of the dispersing agent are probably adsorbed on the clay particle, thus increasing the negative charge[68] and the over-all net charge of repulsion. In addition, dispersing agents also increase the exchange activity, thereby increasing the hydration by building up the double layer about the clay particle. Presumably, then, dispersing agents work in two ways, by increasing the thickness of the liquid film about the clay particles and also by increasing the charge on the clay particles, both of which reduce the mutual attraction between the particles. Because of the weaker attraction, the particles become more readily mobile, and the clay dispersion has greater fluidity.

When alkaline dispersion agents are first added to clay, there is no change in *p*H while sodium ions are replacing hydrogen ions on the flocculated clay particle. After base exchange is complete, the concentration of free hydroxyl ions increases, thereby resulting in a sudden rise in *p*H and a preferential adsorption of hydroxyl ions on the clay particle.[69] As a rule, neutral or acid salts do not make good dispersing agents, because acids are formed as a result of base exchange. Disodium hydrogen pyrophosphate is an exception, since it produces deflocculated clay suspensions under fairly acid conditions. Most deflocculation agents result in a *p*H of 6 to 7, but additional alkali (sodium carbonate or sodium hydroxide) up to a *p*H of 7 to 9 generally results in a further reduction in the viscosity.[70, 71]

Clays vary considerably in the ease with which they can be dispersed. As a general rule, clays of low surface activity yield suspensions of low viscosity and require only a small amount of deflocculating agent for minimum viscosity. On the other hand, clays of high surface reactivity tend to produce viscous, thixotropic suspensions and require high percentages of deflocculating agent for minimum viscosity. In this connection, Sheets[72] points out that less dispersing agent is required for minimum viscosity with a hydrogen clay than for a clay containing exchangeable cations, because exchangeable cations tend to react with the anion of the dispersing agent.

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[67] G. H. Sheets, *Paper Trade J. 116,* No. 3: 22–30 (Jan. 21, 1943)

[68] *J. Phys. Chem. 44,* 1–12 (1940)

[69] B. K. Asdell, *Paper Ind. 29,* No. 7: 1035–1042 (Oct., 1947)

[70] "Kaolin Clays and Their Industrial Uses," Chapter 13, J. M. Huber Corp., New York, N. Y. (1949)

[71] W. R. Willets, *Tappi 33,* No. 4: 201–208 (Apr., 1950)

Flocculation of Clay. Some agents act oppositely to dispersing agents, that is, they thicken clay suspensions. Cations, in general, flocculate clay, and the flocculating tendency in decreasing order is as follows for anion-dispersed clay: H^+, Al^{+++}, Ca^{++}, Ba^{++}, Mg^{++}, K^+, and Na^+. The order follows the usual lyotropic series, with the exception of the hydrogen ion (H^+), which has a disproportionately greater flocculating effect because of its small size, which permits it to come into very intimate contact with the clay particle. Alum causes rapid flocculation of clay suspensions, due to Al^{+++} replacing Na^+, whereby the greater charge and adsorption of Al^{+++} reduces the negative charge on the particle. Further addition of alum increases the concentration of Al^{+++} in the intermicellar solution and, at the same time, increases the H^+ concentration, thereby bringing the suspension to the isoelectric *p*H.

Clays which contain polyvalent cations (e.g., calcium, magnesium, or aluminum) are difficult to disperse. Commercial clays usually contain a small amount of soluble salt, but this should be kept to a minimum, since it interferes with the proper dispersion of the clay. Precipitated calcium carbonate sometimes contains enough free lime to cause thickening of clay suspensions, and satin white has been known to cause trouble in the same way. Adhesives sometimes contain sufficient cations to cause trouble. Dicyandiamide is effective in reducing the flocculation which occurs in the presence of salts and is used in this way for controlling the viscosity of oil-well drilling muds.[73]

Calcium Carbonate

Calcium carbonate is a pigment which is becoming of increasing importance to the paper industry. Two types are used, precipitated carbonate and water-ground carbonate.

Calcium carbonate is used for the filling of paper and for paper coating. Increasing amounts are being used for coating, usually in combination with clay, where the carbonate tends to increase the brightness, opacity, and ink receptivity of the clay. The early calcium carbonate pigments were coarse and poor in color, but improved products have been made in recent years.

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[72] G. H. Sheets, *Paper Trade J. 116*, No. 3: 22–30 (Jan. 21, 1943)
[73] Bulletin No. 18, "For Instance," American Cyanamid Co. (1946)

Calcium carbonate has at least two, and possibly three, allotropes. The two common ones are calcite, which is trigonal, and aragonite, which is orthorhombic. The water-ground (natural) carbonates are entirely calcite, whereas the precipitated grades contain some aragonite. The products are non-hygroscopic and contain no water of crystallization. The particle size usually averages 2 to 3 microns, but often is as high as 7 to 8 microns, depending upon the grade. Certain of the high finish carbonates for paper coating are much finer than this, containing many particles less than 0.1 micron in size. The brightness of calcium carbonates is generally in the range of 93 to 98.

Calcium carbonate disperses readily in water, and dispersing agents such as are necessary with clay are not always required. Precipitated calcium carbonate produces somewhat thicker slurries than the water-ground product, and dispersing agents are required at concentrations over 30 to 35% solids. Casein is one of the best dispersing agents, and slurries up to 70% solids can be prepared using a small amount of casein. Oxidized starches and sodium hexametaphosphate make good dispersing agents, although the effect obtained with polyphosphates is not as permanent as that obtained with casein. Special dispersing methods, which will be described later, are necessary in order to lower the naturally high adhesive demand of calcium carbonate.

Calcium carbonate is relatively insoluble in water. The *p*H of carbonate slurries is generally in the neighborhood of 7.0 to 7.5, although it may be as high as 9.0 to 10.0 for some of the precipitated grades. Calcium carbonate has the disadvantage of breaking down in the presence of dilute acids, thereby liberating carbon dioxide.

Precipitated Calcium Carbonate. Precipitated calcium carbonate can be made by several different methods: (*1*) by burning limestone to lime, which is then dissolved in water and precipitated as calcium carbonate by adding either carbon dioxide or sodium carbonate; (*2*) by the metathesis of calcium chloride and sodium carbonate; or (*3*) as a by-product of soda pulp mill operation. The last method generally produces a product of lower purity than the other methods because of contamination with silicates, iron, manganese, and other impurities which are picked up in the pulping operations. Lime mud from the sulfate process may be used, but considerable processing is necessary to remove the blue-green color. Some of the finer precipitated carbonates are sold in pulp form, but most are shipped in the dry state.

In all the above processes, it is necessary to maintain careful control of the temperature, concentration, and amount of agitation during precipitation in order to obtain a product of suitable and uniform particle size.

Sears and Kregel[74] found that the properties of precipitated calcium carbonates often vary greatly, depending upon the conditions of precipitation. The particle size can be controlled in the carbon dioxide process by controlling the following variables:[75] (*1*) type of lime; (*2*) the degree of agitation in reaction tanks (the more violent the agitation, the finer the particles); (*3*) the temperature (the lower the temperature, the finer the particles); and (*4*) the rate of carbonation. Lime quality has an important influence on the purity of the final pigment.

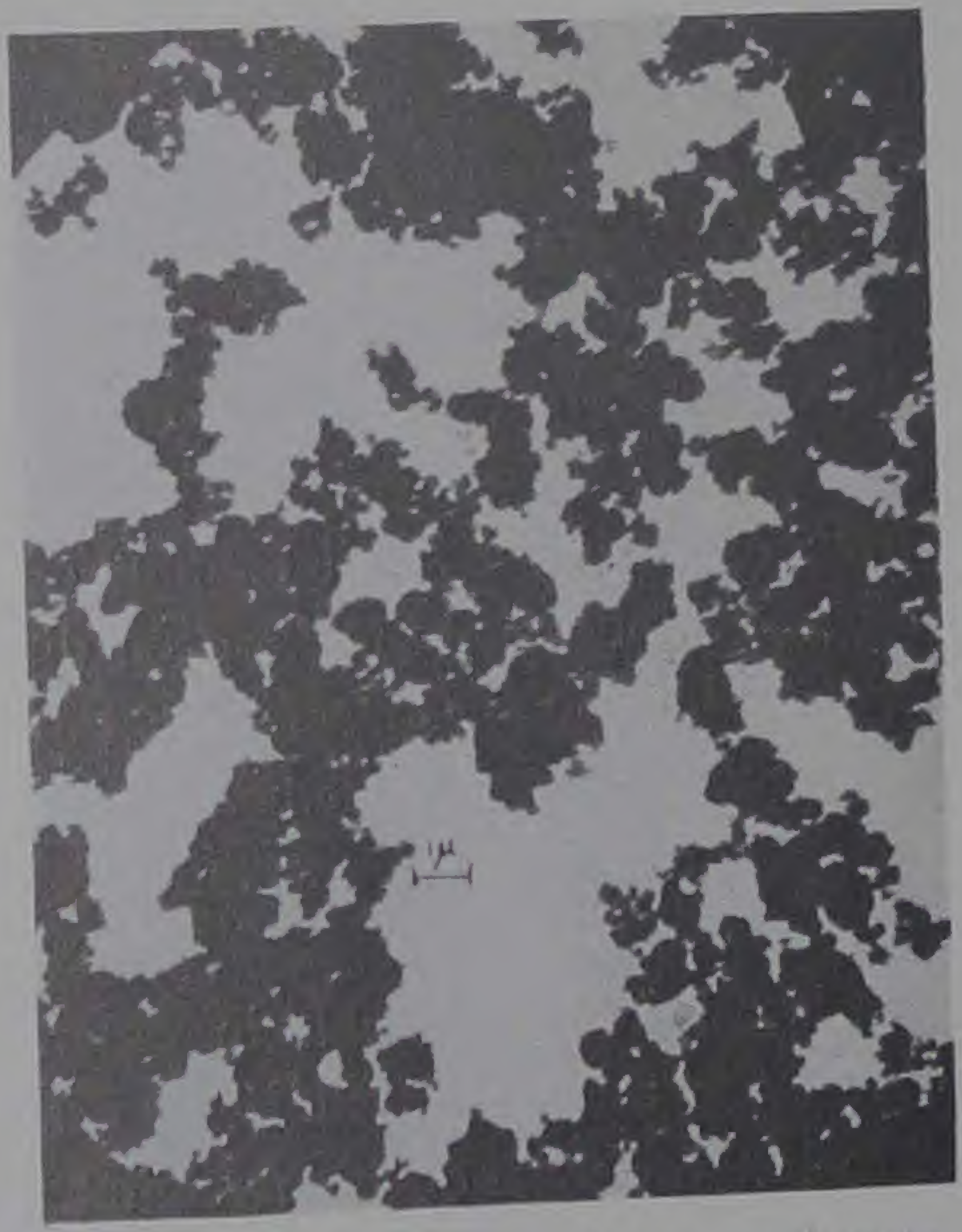

Fig. XVIII-12. Precipitated calcium carbonate (3000×) (courtesy Powdered Materials Research Laboratories).

Precipitated calcium carbonate is composed of tiny prisms interlocked and held together by crystalline forces, giving the particle a porous interior and a rough exterior. The particles are roughly 0.5 micron in width and 2 microns in length, but due to their unusual shape, they present a large surface area. The surface area of precipitated carbonates runs from 10 to 50 sq.m. per gram where the effective diameter of the clusters range from 0.5 to 2.0 microns.[76] Because of their porous character, precipitated calcium carbonates have high oil and water absorption and have a high adhesive requirement when used in coated papers.[77] An electron micrograph of precipitated calcium carbonate is shown in Figure XVIII-12. Residual chemicals from the reaction process are held in the porous internal structure. For example, if lime or sodium hydroxide is used as one of the reactants, the final product is likely to retain these materials, giving the product a high *p*H, unless the lime mud is neutralized with acids or acid salts. If the reaction between calcium chloride and sodium carbonate is used, an excess of calcium chloride (an acid salt) can be maintained during precipitation to prevent any free alkalinity in the finished product.

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[74] G. R. Sears and E. A. Kregel, *Paper Trade J. 114,* No. 12: 139–145 (Mar. 19, 1942)

[75] H. R. Davidson, *Pulp Paper Mag. Canada 46,* No. 3: 205–211. Sixth Wartime Issue (1945)

[76] Private communication. A. R. Lukens, Powdered Material Research Laboratories, Cambridge, Massachusetts (Dec. 15, 1948)

[77] A. R. Lukens, C. G. Landes and T. G. Rochow, *Paper Trade J. 112,* No. 15: 183–190 (Apr. 10, 1941)

Calcium carbonate pigments are available in dull, medium, and high finishing grades. However, these classifications are only relative since probably no calcium carbonate is truly a high finishing pigment in the sense that refined clays are. The properties of the different grades of calcium carbonate are given in Table VI.[78] The dull finishing grades include the water-ground grades. The high finishing types must be dispersed at relatively low solids because of their high water absorption.

TABLE VI

PARTICLE SIZE DISTRIBUTION (IN PER CENT) OF DIFFERENT GRADES OF CALCIUM CARBONATE

Type	Approximate Ingersoll gloss	Average particle size, microns	Particle size range, microns		
			1 and under	1–5	5–10
Dull finishing	28	3–5	2%	88%	10%
Medium finishing	35	0.5–2	5	95	0
High finishing	50	Under 1	63	36	1

Ground Calcium Carbonate. Ground calcium carbonates are made by water-grinding a pure natural limestone rock (at least 98% carbonate), and then mechanically separating the ground product into suitable particle size. French chalk is considered to be the highest grade. Ground carbonates, in contrast to precipitated carbonates, are composed of solid fragments with a relatively smooth surface. An electron micrograph of water-ground calcium carbonate is shown in Figure XVIII-13. The surface area of water-ground carbonates is about 4 to 5 sq.m. per gram, and the median diameter is about 0.8 micron.[76] The brightness is about 90, compared with about 95 to 97 for the precipitated grade, and the specific gravity about 2.2 to 2.7.

Titanium Pigments

Titanium pigments are used in paper coating in the form of titanium dioxide and in the form of the composite pigments, i.e., mixtures of titanium dioxide and other white pigments. Titanium dioxide is available in two modifications, the rutile and anatase. The rutile has a more compact crystal structure and a higher refractive index (2.70) than the anatase (2.55). The anatase is most commonly used for papermaking, but the rutile form is becoming of increasing importance. It has approximately one-third greater hiding power than the anatase form. The brightness is 97 to 98, and the specific gravity about 3.88.

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[78] TAPPI Monograph No. 7, "Pigments for Paper Coating," Tech. Assoc. of the Pulp & Paper Industry, 122 East 42nd St., New York, N. Y. (1948)

Extended or composite titanium pigments consist of mixtures of titanium dioxide with either barium, calcium, or magnesium pigments. Titanium-barium pigment contains 70% barium sulfate; titanium-calcium pigments contain 70% calcium sulfate; and titanium-magnesium pigment contains 70% magnesium silicate. Composite pigments can be prepared by precipitation of the extender pigment on the titanium dioxide, or by mixing the titanium dioxide and extender pigment together either before or after calcination.

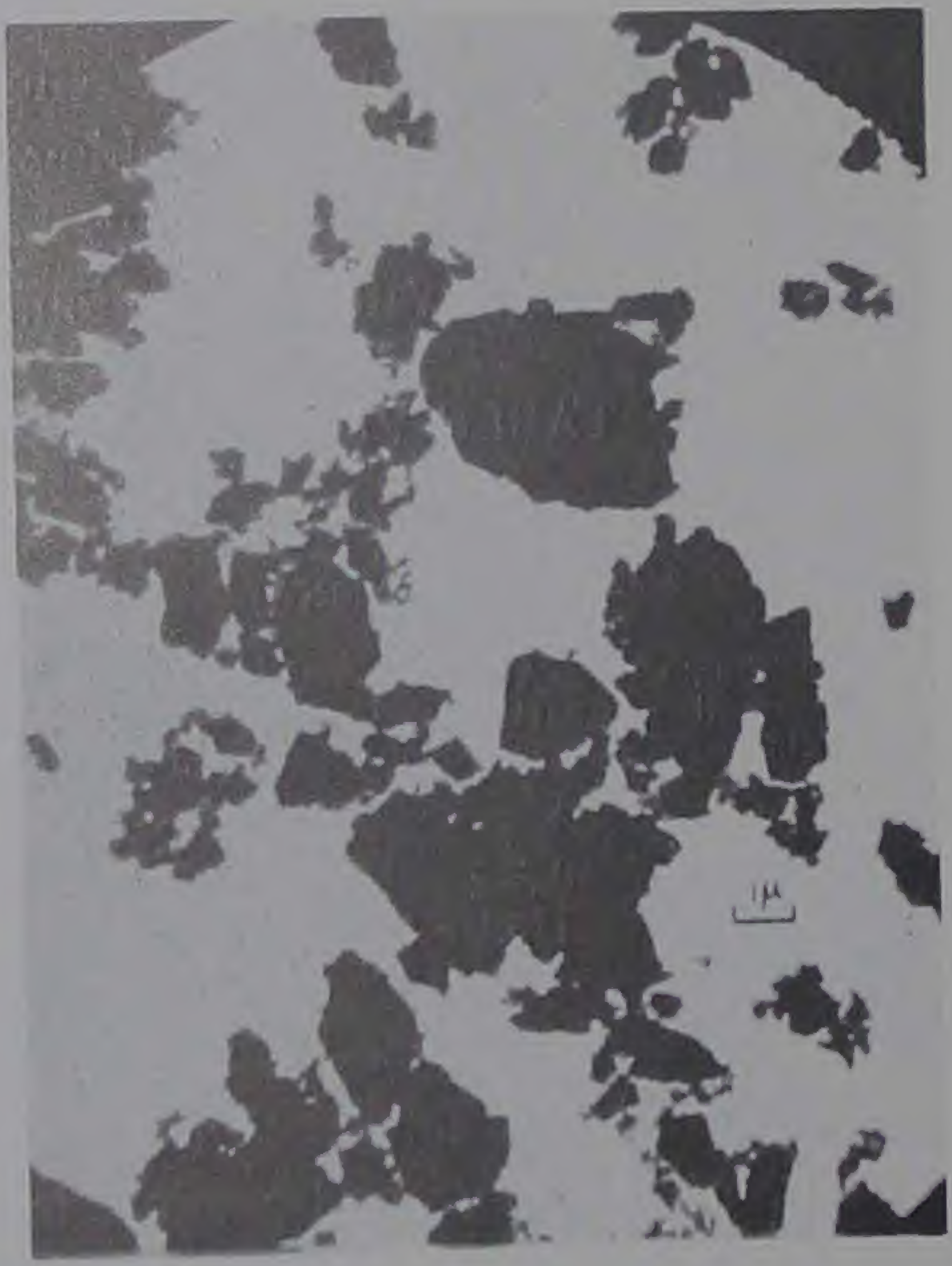

Fig. XVIII-13. Water ground calcium carbonate (3000×) (courtesy Powdered Materials Research Laboratories).

Titanium pigments are used in coating to increase the opacity, brightness, and whiteness of clay coatings. They also increase the smoothness and finish of the coating. The gloss is ordinarily not affected. As a rule, titanium pigments form a minor part of the pigment furnish, but their effect on the properties of the coated paper is appreciable because of their exceptionally high brightness and opacifying power. Titanium pigments are especially useful in light-weight papers which are deficient in opacity. Because of their high index of refraction, titanium pigments are widely used in coatings which are impregnated with wax. For the same reason, coatings containing titanium pigment undergo comparatively little loss of opacity when printing inks strike into the paper, thereby helping to alleviate a common printing complaint known as "strike through."

Preparation of Titanium Dioxide. Titanium dioxide is not mined as such, but rather is obtained from ilmenite ore, which has the approximate formula $FeOTiO_2$. The iron is present in both the ferrous and ferric states. The titanium dioxide content of ilmenite ore varies from 35 to 55%.

Prior to World War II, most of the ilmenite was obtained from India, but since the war, domestic deposits have been opened up. At the present time, New York, New Jersey, Florida, North Carolina, Virginia, and Wyoming are the principal sources of domestic ilmenite.

In the production of titanium dioxide from ilmenite ore, the ore is first dried, then pulverized and reacted with strong sulfuric acid to form a dry cake. This cake is then dissolved in warm water to produce a solution of titanium sulfate and iron sulfates. This solution is clarified to remove extraneous materials, and the solution is then cooled so that some of the ferrous sulfate (copperas) crystallizes out. The solution is boiled to hydrolyze the soluble titanium sulfate to the insoluble hydrated oxide, which is then filtered and washed to lower the iron content below 0.01%. The next step is calcination at a temperature between 800 to 1100° C. to change the amorphous titanium hydrate to the cryptocrystalline dioxide, having a high refractive index and a purity of 98% TiO_2. Finally, the product is milled in the wet or dry state to break down aggregates. The properties of the final pigment depend on the purity of the ore, concentration and acidity of the solution, the presence of a suitable number of nuclei for seeding during precipitation, and the temperature of calcination. Pigments from unseeded solutions tend to be coarse in size,[79] and to be agglomerate, rather than crystalline, so that they are not an article of commerce. The calcination operation is probably the most important operation in determining the physical properties of the pigment. As the calcining temperature is increased above a temperature of 850° C., the size of the pigment particles becomes larger, as shown by reduced oil absorption.

Properties of Titanium Pigments. Titanium dioxide is available in both water-dispersible and oil-dispersible grades. The water-dispersible (anatase) grades are readily suspended in water at concentrations of 75% solids without the use of dispersing agents. The oil-dispersible (rutile) grades require the use of dispersing agents, such as sodium hexametaphosphate or gum arabic, the latter being the most effective. Sodium silicate is not suitable as a dispersing agent, because it reacts with titanium.

The average particle size of titanium dioxide is about 0.3 to 0.6 micron, and the particles are uniform and roughly spherical in shape. A photograph of a flocculated and deflocculated titanium dioxide suspension is shown in Figure XVIII-14. The results in Table VII, taken from work of Martin,[80, 81] show the range of particle size of several different titanium pigments.

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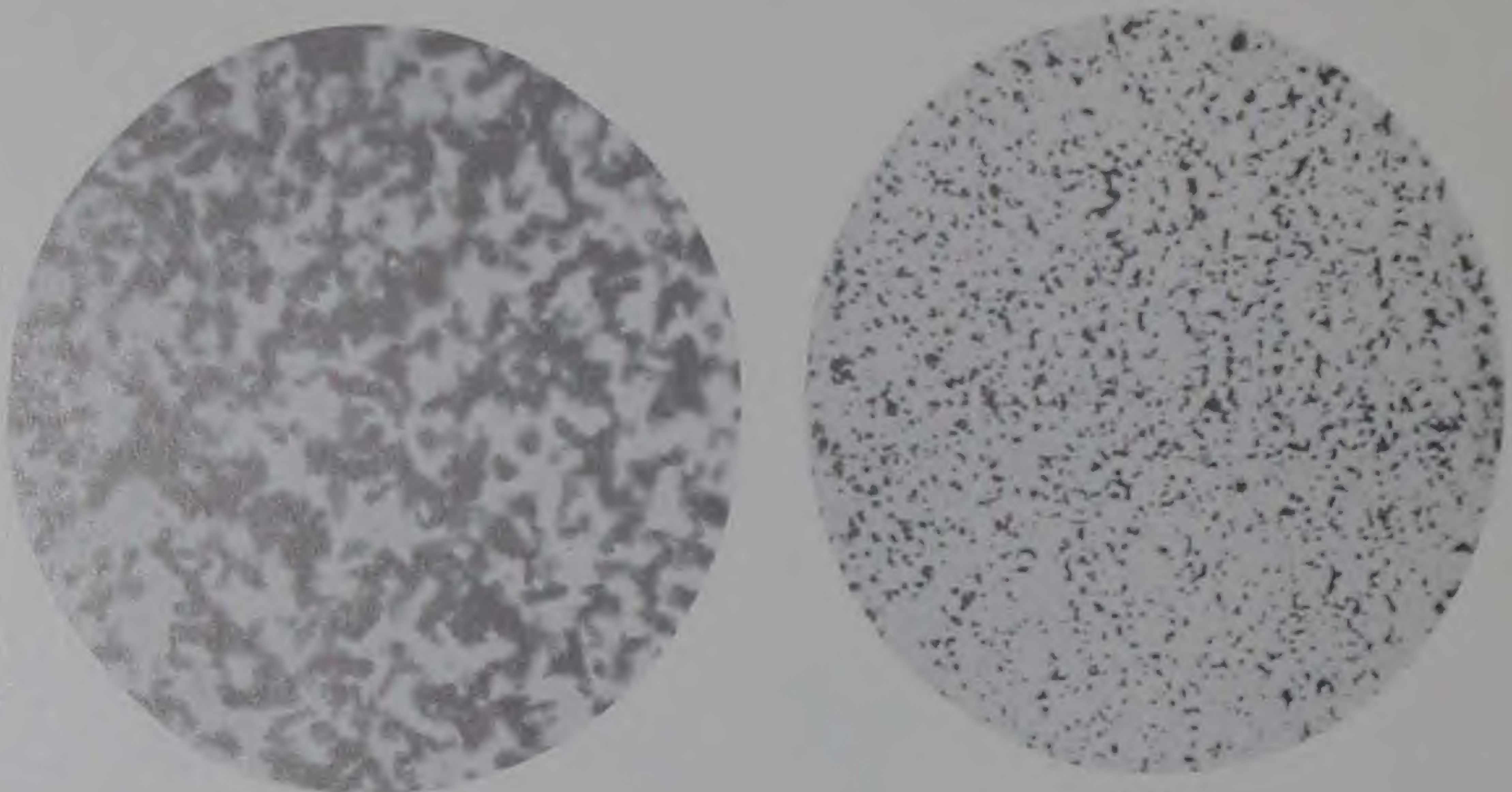
[79] L. T. Work, S. B. Tuwiner and A. J. Gloster, *Ind. Eng. Chem. 26,* No. 12: 1263-1268 (Dec., 1934)



(*A*) (*B*)

Fig. XVIII-14. Titanium dioxide flocculated (*A*) and deflocculated (*B*) (600×) (photographs by Mr. Harry Green, courtesy Interchemical Corporation).

TABLE VII

Particle Size Distribution of Titanium Dioxide
(Water-Dispersing Types)
By Beaker type centrifuge method

Size interval, microns	Percentage of total					
Over 1.0	1.3	1.2	6.5	2.0	2.5	0
1.0–0.5	9.7	6.3				
0.5–0.4	19.5	25.5	17.5	1.3	5.3	0.8
0.4–0.3	18.8	16.0	28.2	36.3	27.5	17.2
0.3–0.2	34.2	35.5	36.4	49.0	52.0	66.0
Under 0.2	16.5	15.5	11.4	11.4	12.7	16.0
Mean surface diameter, microns	0.28	0.28	0.29	0.26	0.26	0.23
Incremental surface area, sq.m./cc. of TiO_2	21.4	21.4	21.0	23.2	23.2	25.9
Solids in final solution, %	0.5	1.0	3.0	5.0	10.0	15.0
Average distance between particles, microns	1.9	1.5	0.92	0.72	0.50	0.39

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[80] TAPPI Monograph No. 7, "Pigments for Paper Coating," Tech. Assoc. Pulp & Paper Ind., New York, N. Y. (1948)

[81] S. W. Martin, "The Determination of Subsieve Particle Size Distributions by Sedimentary Methods," pp. 66–69, Am. Soc. for Testing Materials, Symposium on New Methods for Particle Size Determination in the Subsieve Range (1941)

The principal titanium pigments used for coating are the anatase titanium dioxide and the rutile titanium dioxide-calcium mixed pigments, made by precipitating 30% rutile titanium dioxide upon 70% of precipitated calcium sulfate. The titanium-calcium pigment is slightly soluble, due to the solubility of the calcium sulfate; this is not a serious disadvantage for paper coating, although it is a disadvantage for use in the filling of paper. The refractive index of titanium-calcium (rutile) is 1.98. This pigment has the highest hiding power of the composite pigments, although it is less than that of pure titanium dioxide. It has a particle size about twice that of pure titanium dioxide, or about 0.5 to 0.8 micron. Titanium (rutile) calcium pigment can replace titanium dioxide in coating in the ratio of about 2.5 parts of the mixed pigment to one part of the pure titanium dioxide without any loss in optical properties.[82] As a general rule, the mixed pigment is cheaper than a combination of the anatase titanium dioxide and clay on an equivalent basis.

Satin White

Satin white is a pigment which has enjoyed rather widespread use in the past. It is not so widely used as formerly because of the relatively high cost and the difficulties in handling. Satin white is used chiefly for its high gloss characteristics and its bright color. It produces a coating which is many times bulkier than a clay coating.[83]

Satin white is used with casein, but is rarely used with starch. It forms a rather viscous coating mixture with casein which tends to increase in viscosity (and may even gel) on standing. Satin white is sometimes difficult to disperse, and consequently it is a wise precaution, when using satin white, to grind the coating mixture to eliminate lumps. The amount and type of alkali used for dissolving casein for use with satin white is an important factor, and generally ammonia, trisodium phosphate, or borax are preferred. When properly made, casein-satin white coatings have a high degree of water resistance.

Satin white is made by reacting hydrated lime and aluminum sulfate (iron-free alum) to form calcium sulfoaluminate, which Sutermeister[84] considers to be best represented by the formula $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$. The solutions are mixed cold (anhydrous sodium sulfate may be added with the alum), and then heated to start the reaction, which is exothermic. The mass becomes quite thick. It may be dewatered on a filter press and sold as a paste containing approximately 70% moisture, or it may be made to contain 30 to 33% "paper dry" solids without dewatering. The conditions of temperature and agitation and the method of addition of ingredients affect the final properties of satin white. Small amounts of gum arabic are added as a stabilizing and dispersing agent. Commercial products are usually quite variable in composition and properties. Satin white should be protected from freezing.

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[82] W. R. Willets, *Tappi 32,* No. 8: 349–356 (Aug., 1949)

[83] J. Phillips, Thesis, "Study of Properties and Structure of Pigment Coatings." New York State College of Forestry, Syracuse, N. Y. (Dec., 1949)

[84] E. Sutermeister, *Paper Ind. 15,* No. 12: 696–698 (Mar., 1934)

The lime used for making satin white should be free of iron, because too much iron in the lime results in a pigment having a slight yellow color. Lime is frequently used in excess, so that the final product is strongly alkaline, usually containing about 17 to 25% lime on an air-dry basis. Because of the alkalinity of the product itself, it is impossible to determine the amount of excess lime by titration. Satin white contains a considerable amount of water which it tends to lose at high temperatures. Heating to 100° C. results in a loss of about 25 to 30% of the air-dry weight, and a further loss occurs if heating is continued at higher temperatures. An electron micrograph of satin white is shown in Figure XVIII-15.

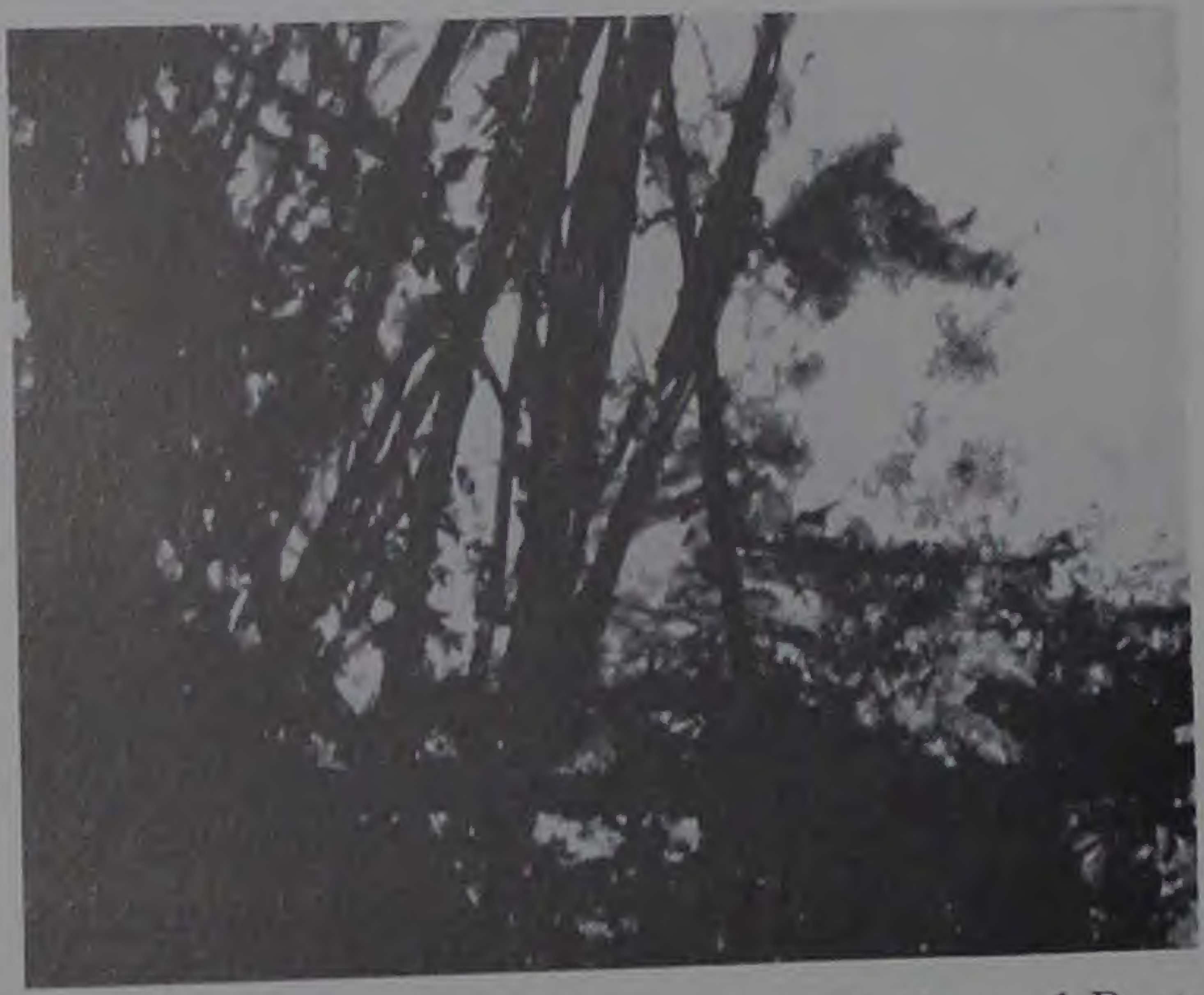

Fig. XVIII-15. Satin white (10,000×) (courtesy Institute of Paper Chemistry).

Zinc Pigments

The most important zinc pigments are zinc oxide, zinc sulfide, and the composite zinc sulfide pigment, lithopone. These pigments are used to some extent in paper coating when a pigment of high refractive index is desired.

Zinc Sulfide. Zinc sulfide is made by passing hydrogen sulfide into a solution of soluble zinc salt. After precipitation, the pigment is filtered, dried, and calcined. During calcination, crystal growth is started and the sulfide is changed from a hydrated material of low refractive index to a crystalline substance of high refractive index (2.37). The growth of crystals starts at a calcination temperature of 450° C. At temperatures higher than about 750° C., there is a tendency to produce excessively large crystals.[85]

Zinc sulfide has a small particle size, the average size being in the neighborhood of 0.3 micron.[86] The particles are uniform and contain practically no individual particles over 1.0 micron. Zinc sulfide is unstable in the presence of acids, tending to liberate hydrogen sulfide at *p*H values of 4.8 or below. The brightness is 94 to 96, and the specific gravity about 4.0.

Certain grades of zinc sulfide are highly luminescent. These grades are calcined at relatively high temperatures, and consequently the particle size is somewhat coarse, ranging from about 1 micron for the fluorescent grades to 5 to 10 microns or more for the phosphorescent grades.[87]

Composite Zinc Sulfide Pigments. Composite zinc sulfide pigments have been known for some time. One product includes a combination of zinc sulfide with precipitated barium sulfate in approximately a 50-50 ratio. Another product includes a combination of zinc sulfide, barium sulfate, and titanium dioxide in the ratio of 25% zinc sulfide, 60% barium sulfate, and 15% titanium dioxide. Lithopone is the oldest zinc sulfide composite pigment; it is made by the coprecipitation of zinc sulfide and barium sulfate from solutions of barium sulfide and zinc sulfate. The final product contains about 30% zinc sulfide and 70% barium sulfate, usually existing as separate discrete units. The refractive index is between 1.84 to 2.00.

Zinc Oxide. Zinc oxide is generally made by burning zinc in air and collecting the oxide in special fabric bags. In one process, pure zinc is burned. In another process, zinc ore is burned in mixture with coal.

Zinc oxide has a high refractive index (2.01) and a good white color. Zinc oxide has an exceptionally high specific gravity, which is in the neighborhood of 5.6. It is soluble in acid solutions and is therefore impractical to use as a filler in the presence of alum. It can be used in paper coating, although it tends to react with casein to cause geling of the coating mixture. Because of these limitations, zinc oxide is not widely used in papermaking.

Barium Sulfate

Barium sulfate is used in the paper industry in two different forms: as the natural mineral product, barytes, or as the artificial product, blanc fixe. Both are used for filling and coating.

Barytes is found in many parts of the United States, in particular, in Mississippi, Georgia, and Tennessee. In preparing the pigment for market, the mineral is first ground and separated into the desired particle size. The pigment is then treated with acid to remove impurities, dried, and reground.

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[85] L. T. Work and I. H. Odell, *Ind. Eng. Chem.* 25, No. 5: 543-549 (May, 1933)

[86] O. Kress and H. M. Cyr, *Paper Trade J.* 96, No. 10: 127-130 (Mar. 9, 1933)

[87] M. A. Heikkila, *Rayon Textile Monthly* 25, No. 6: 295-296 (June, 1944)

Barytes occurs in both the amorphous state and crystalline (orthorhombic) state, and generally has an average particle size of 2 to 5 microns.

Blanc fixe can be made from either barytes or witherite, a barium carbonate ore found in England and Europe. When preparing blanc fixe from barytes, the finely ground mineral is calcined with coal or coke to reduce the sulfate to barium sulfide. The soluble sulfide is then leached from the ash and precipitated as the sulfate by adding sodium sulfate or sulfuric acid to the liquor. In some cases, hydrochloric acid may be used for leaching the ash, and the resulting barium chloride then is precipitated with sodium sulfate or sulfuric acid. If witherite (barium carbonate ore) is used as the raw material, the ore is treated with hot hydrochloric acid to form barium chloride, which is then filtered and treated with sulfuric acid or sodium sulfate to precipitate barium sulfate. Another grade of blanc fixe is obtained as a by-product in the manufacture of hydrogen peroxide from barium peroxide.

Blanc fixe has a finer particle size, is more uniform, and contains less grit than barytes. It is sold in both dry and paste form, the latter containing about 35% water. The average particle size of blanc fixe is in the neighborhood of 0.5 to 2.0 microns.

Blanc fixe is used for the coating of high-grade photographic paper, where it produces a coating of high finish, satiny feel, and high brightness. It is also used in special grades of coated chart papers where a metal stylus is employed in place of pen and ink for marking on the coating. Coatings produced from blanc fixe are denser and less porous than coatings produced from other pigments. Blanc fixe is used in making lithopone, a zinc-barium pigment.

Both forms of barium sulfate have high brightness (95 to 98%) and a very high specific gravity (4.3–4.5). The refractive index is about 1.64. The pigment is insoluble in water and resistant to acids and alkalies. The *p*H of barium sulfate suspensions is generally around 3.5

Calcium Sulfite

Calcium sulfite is a white pigment which has found some use in the filling and coating of paper. It is an alkaline pigment (*p*H of 8–9) and is attacked by strong acids. The specific gravity is 2.51, and the refractive index is 1.5. The brightness varies from 92 to 96. The pigment contains about 7% water of crystallization.

There are several processes for producing calcium sulfite, and many of these are patented.[88–92] One process, which is said to produce a grade

[88] U. S. 1,984,188 (Dec. 11, 1934)
[89] U. S. 2,191,465 (Feb. 27, 1940)
[90] U. S. 2,210,405 (Aug. 6, 1940)
[91] U. S. 2,375,786 (May 15, 1945)
[92] U. S. 2,413,321 (Dec. 31, 1946)

suitable for the filling of paper, consists of passing hot sulfur dioxide gas (17–18% sulfur dioxide) through a spray of milk of lime at 50 to 60° C. The pigment contains flat plates and has an average particle size of around 6.5 microns. A modified product is obtained by treating a slurry of calcium sulfite as prepared above with sulfur dioxide gas. This reduces the particle size and improves the product for paper coating. Another process consists of treating calcium carbonate with sulfurous acid.

Calcium sulfite has not been used to a great extent for paper coating because of its high adhesive demand and low gloss properties. However, it is possible to reduce the adhesive demand by mechanical or chemical treatment of the pigment so that only about 20% starch is necessary to obtain a coating which passes a No. 6 wax. Calcium sulfite must be made up in lower solids than clay because of its high water absorbing properties. It can be dispersed with the aid of about 0.75 to 1.0% of sodium hexametaphosphate on the weight of the pigment. Coatings made with calcium sulfite have high brightness and good ink absorbency.

Calcium Sulfate

Calcium sulfate is used in the paper industry in two forms: the natural product, gypsum ($CaSO_4 \cdot 2H_2O$), and the artificial product, known as pearl hardening, pearl white, pearl finish, crown filler, or alabastine. The natural product, gypsum, is mined, ground, and sold as a fine powder. It has plate-like crystals. Artificial calcium sulfate is generally made by reacting solutions of calcium chloride and sodium sulfate. The final product contains a considerable amount of free water. It may occur in the form of flat plates or needle-shaped crystals, depending upon the amount of combined water.

A calcined gypsum is made by heating to remove water of crystallization. This product is sometimes known as pearl filler, calopone, or alabaster. It generally has a finer particle size than the natural gypsum. This is one of the most highly soluble pigments (0.2 part soluble in 100 parts of water).

Diatomaceous Silica

Diatomaceous silica (known also as kieselguhr or infusorial earth) is a type of silica which is obtained from the fossil remains of microscopic plant life known as diatoms. It is mined as siliceous skeletons of diatoms, which are found in diatomaceous earth. The material is chemically treated and air-separated, and is sold as a very fine, white, grit-free product. A calcined product with special properties is also available.

The particles of diatomaceous silica are amorphous and quite fragile and are characteristically diverse in size and shape. The average size is about 10 microns. Diatoms, if acicular, are about 1 to 5 microns in diameter and 10 to 50 microns in length, and if circular, they have a mean diameter of approximately 5 microns. Because of their highly porous nature, the particles have an enormous specific surface which approaches 10 to 50 sq.m. per gram.[93]

Diatomaceous silica has a brightness (G.E.) from 65 to 95. The calcined product has an appreciably higher brightness than the regular product. The moisture content varies from 5 to 7% for the regular product to about 1% for the calcined product.

Diatomaceous silica is sometimes used in small quantities in paper coating to reduce gloss and to increase the resistance of the coating to blackening on calendering. In high concentrations, it makes the coating very abrasive.

Luminescent Pigments

Some inorganic pigments possess photoluminescent properties, that is, they are capable of absorbing radiant energy and converting it into visible light. There are two types of luminescent pigments: (*1*) fluorescent pigments, which emit light only when the exciting light source (i.e., black light) is shining on the pigmented surface, and (*2*) phosphorescent pigments which continue to emit light after the light source (either black light or visible light) is removed. The latter have an afterglow of two to three hours for some pigments, and up to twenty to twenty-five hours for others.

Commercial luminescent pigments are usually sulfides of zinc, cadmium, strontium, or calcium. These are manufactured by mixing the pure sulfides with small amounts of activators and then heating at high temperature in special furnaces. The phosphorescent pigments of short afterglow are specially prepared zinc sulfides or combinations of zinc and cadmium sulfides. The phosphorescent pigments of long afterglow are special combinations of calcium and strontium sulfides. The average size of fluorescent pigments is about 1 micron, whereas the size of phosphorescent pigments is generally about 5 to 10 microns.[94]

Luminescent pigments are being used in the production of special map papers, instrument dials, display papers, gift and decorative papers, and safety papers. The pigments can be used for filling, pigment coating, or lacquer type coatings. The fluorescent pigments and the phosphorescent pigments of short afterglow (zinc and cadmium sulfides) can be used in regular filling and pigment coating. The long afterglow phosphorescent pigments cannot be used for filling or pigment coating because of their sensitivity to water, and consequently the use of these is limited to lacquer type coatings. The coarse size and relatively high cost limit the use of luminescent pigments.

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[93] Private communication. A. R. Lukens, Powdered Material Research Laboratories, Cambridge, Massachusetts (Dec. 15, 1948)

[94] M. A. Heikkila, *Rayon Textile Monthly 25*, No. 6: 296–297 (June, 1944)

Colored Pigments

Most of the pigments used in paper coating are white, but in some cases, it is desirable to use colored pigments. These may be added to the regular clay coating mixture, or they may be used as the only pigment in the coating mixture.

Colored pigments are used where permanency is required. The pigments commonly used are:

Yellows—chrome yellows (barium and zinc) and iron oxides.
Blues—ultramarines, iron blues, cobalt blues.
Browns—umbers and iron oxides.
Greens—cobalt green, Malachite green, emerald green.
Reds—sienna, red lead, Indian red, orange lead.
Blacks—lampblack, carbon, and bone black.

Colored pigments should be finely dispersed in order to obtain the highest possible color strength. In some cases, trouble is experienced with small, hard lumps of color producing streaks in the coating. These colored particles are so small that they are passed through the screens used for removing coarse material from the coating mixture. In order to avoid this trouble, it is best to disperse the pigment in water or in a mixture of alcohol and water before adding to the coating mixture. With some colored pigments, it is necessary to use large amounts of water, and this should be taken into consideration in calculating the solids content of the coating mixture. Grinding of the coating mixture in an ink or colloid mill also helps to break up any undispersed particles.

Colored lakes, both in dry and paste form, are widely used in coating. These are available in a wide range of colors and produce deep-colored coatings of excellent brilliance.

Adhesive Demand of Coating Pigments

One of the most important properties of a pigment is its adhesive demand, i.e., the amount of adhesive required to bind the pigment to the paper so that it will not dust on calendering or pick during printing. A low adhesive demand is a desirable pigment property because it means that a low percentage of adhesive will be required in the coating formula to meet the strength demand of the coated paper. The strength which is obtained with a definite amount of any given adhesive is determined by a complex set of factors which include the characteristics of the raw stock and the total solids of the coating mixture, as well as the properties of the pigment.

In studying the adhesive demand of different pigments, coated sheets are made by hand, using varying percentages of adhesive, and then these coatings are tested for strength with a series of special waxes (see section on "Evaluation of Coated Papers"). In general, the strength of the coating increases as the amount of adhesive is increased, but the relation between the wax pick test and the amount of binder used in the coating is not a linear function. Usually the wax number increases rapidly with an increase in the amount of binder in the range of low wax number (i.e., low coating strength), but the slope decreases in the range of higher strength, and the curve eventually levels off. Hughes and Roderick[95] found that precipitated calcium carbonate differs from other pigments in this respect in that the wax number increases more rapidly in the ranges of higher wax number than some of the other pigments. The comparative adhesive demand of different pigments depends somewhat upon the type of adhesive used as the binder. Comparative adhesive demands for several different pigments based upon the percentage of casein required for the coated paper to pass a No. 5 Dennison wax are shown in Table VIII.[96]

TABLE VIII

COMPARATIVE ADHESIVE DEMANDS OF SEVERAL PIGMENTS BASED ON AMOUNT OF CASEIN REQUIRED FOR COATED PAPER TO PASS A NO. 5 DENNISON WAX

Type of pigment	Casein required, %
Regular clay	12–13
High-finish coating clay (domestic)	12–14
High-finish coating clay (English)	13–17
Water-ground natural calcium carbonate	9–10
Precipitated calcium carbonate	20–30
Satin white	45–55

Curves showing the casein demand of different pigments over a wide range are shown in Figure XVIII-16.

It can be seen from Table VIII that regular coating clay and water-ground calcium carbonate have a comparatively low adhesive demand, whereas precipitated calcium carbonate and satin white have a comparatively high adhesive demand.

In a certain particle size range, English coating clays have a much higher adhesive demand than American clays, often requiring up to 25 to 30% more adhesive. Titanium has a slightly higher adhesive demand than clay. There are no available figures on the adhesive demand of blanc fixe, although in general, it appears to have a slightly lower adhesive demand than clay. Comparative adhesive demands may be somewhat different when comparisons are made in the range of very high wax number, e.g., clay and precipitated calcium carbonate may have the same adhesive demand when compared under conditions of high coating strength. The adhesive demand depends somewhat upon the method of "make down" of the pigment, particularly in the case of calcium carbonate.

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[95] A. E. Hughes and H. F. Roderick, *Paper Trade J. 109*, No. 11: 128–133 (Sept. 14, 1939); *110*, No. 26: 346 (June 27, 1940)

[96] A. R. Lukens, C. G. Landes and T. G. Rochow, *Paper Trade J. 112*, No. 15: 183–190 (Apr. 10, 1941)

One of the most important factors affecting the adhesive demand is the average particle size of the pigment. In general, fine particle size clays require more adhesive than the coarser grades of clays,[97] because of the greater specific surface which must be covered with adhesive. Kirkpatrick[98] has pointed out, however, that surprisingly enough this does not hold true with domestic clays. On a comparative basis, different grades of calcium carbonate have the following adhesive demands: dull finishing (large particle size), 10%; medium finishing (medium particle size), 25%; and high finishing (small particle size), 35%.[99] Pigments containing large particles tend to dust more on calendering because of the tendency of the heavy calender rolls to crush or shatter large aggregates.

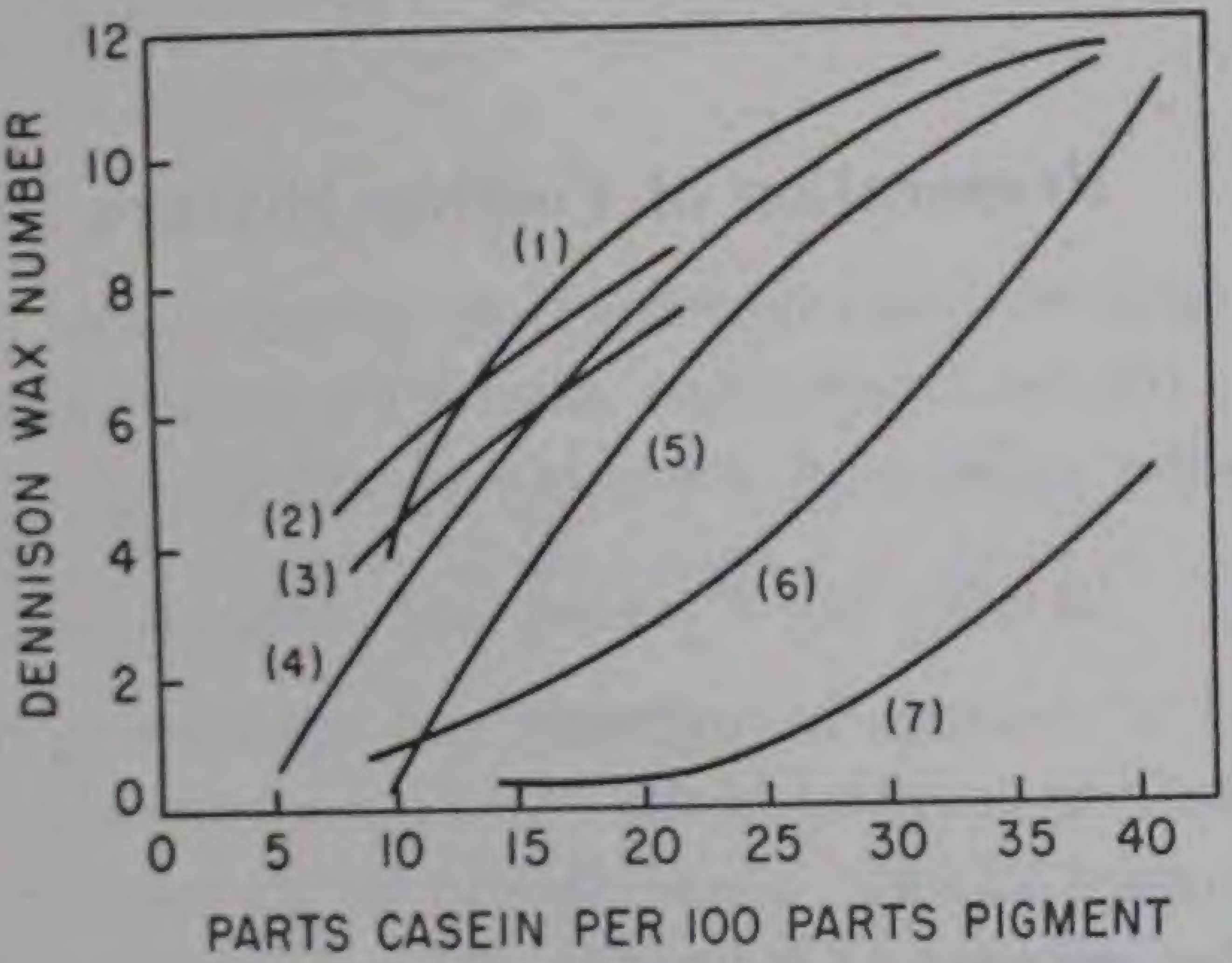

Fig. XVIII-16. Comparative adhesive demands of different pigments.[95] (1) Titanium dioxide, (2) lithopone, (3) blanc fixe, (4) domestic clay, (5) English clay, (6) calcium carbonate, and (7) satin white.

Very probably the particle size distribution, as well as the average size of the particles, is also important in determining the adhesive demand of the pigment. From a theoretical standpoint, a pigment containing particles of different sizes should require less adhesive than a pigment composed of particles of uniform size, even though the average size is approximately the same in both cases. The pigment containing particles of varying sizes should pack better and thus leave smaller pores between the individual par-

[97] R. D. McCarron and B. W. Rowland, *Paper Trade J. 96,* No. 22: 272–276 (June 1, 1933)

[98] W. A. Kirkpatrick, private communication to the author (June, 1950)

[99] TAPPI Monograph No. 7, "Pigments for Paper Coating," Tech. Assoc. Pulp & Paper Ind., New York, N. Y. (1948)

ticles to be filled with adhesive. Such a concept is analogous to that used in concrete mixing, where the engineer chooses an aggregate of rock of varying sizes in order to strengthen the concrete. However, it has been reported that such compositions tend to produce a mottled finish in coated papers.

The amount of adhesive required in blends of two or more pigments is not always the arithmetic average of the adhesive demands of the pigments involved. In some cases, the amount required for the mixture is far less than would be expected. For example, Roderick and Hughes[100] point out that a blend of clay and precipitated calcium carbonate containing 10 to 25% of carbonate has almost the same adhesive demand as straight clay, although calcium carbonate by itself has a considerably higher adhesive demand than clay.

Preparation of Coating Mixture

After the pigment dispersion has been prepared and the adhesive dissolved in water, the next important step is the preparation of the coating mixture (or coating color, as it is sometimes called).

Mixing the Pigment and Adhesive

The method of mixing the pigment and adhesive is important in determining the working qualities of the coating mixture and the properties of of the finished coated paper. There should be an intimate mixture of the adhesive with the pigment. Ordinarily, the adhesive solution is prepared separately and cooled before being added to the pigment slurry, but in the case of some starches, best results are obtained if the starch solution is added to the pigment slurry while still hot, or in some cases, by cooking the starch and pigment together.[101]

Mechanical grinding of the coating mixture in a colloid mill, homogenizer, or ink mill is one way of insuring a more intimate mixture of the adhesive and pigment, and thereby bringing the coating mixture to equilibrium more rapidly. Grinding in this manner increases the bonding strength obtained with some starches, particularly those which do not disperse very well and have low bonding strengths. Grinding generally lowers the viscosity of the coating mixture. Grinding also breaks up aggregates (undisintegrated) pigment particles which, if allowed to remain in the coating mixture, would cause dusting on the calenders and produce surface irregularities in the coating. It should be emphasized that these special dispersing machines are not used in all coating mills; in many cases, their use is not warranted, since a heavy-duty mixer gives all the mixing which is necessary. Some of these dispersing machines have very serious operating disadvantages, such as high cost of operation, excessive wear on parts, and incorporation of foam in the coating mixture. A special mixer, known as the Rafton mill, consists of a very high speed circular saw which strikes a jet of the coating slurry projected into the path of the saw.

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[100] H. F. Roderick and A. E. Hughes, *Paper Trade J. 113*, No. 17: 215–216 (Oct. 23, 1941)

[101] H. T. Ruff, U. S. 2,140,394 (Dec. 13, 1938)

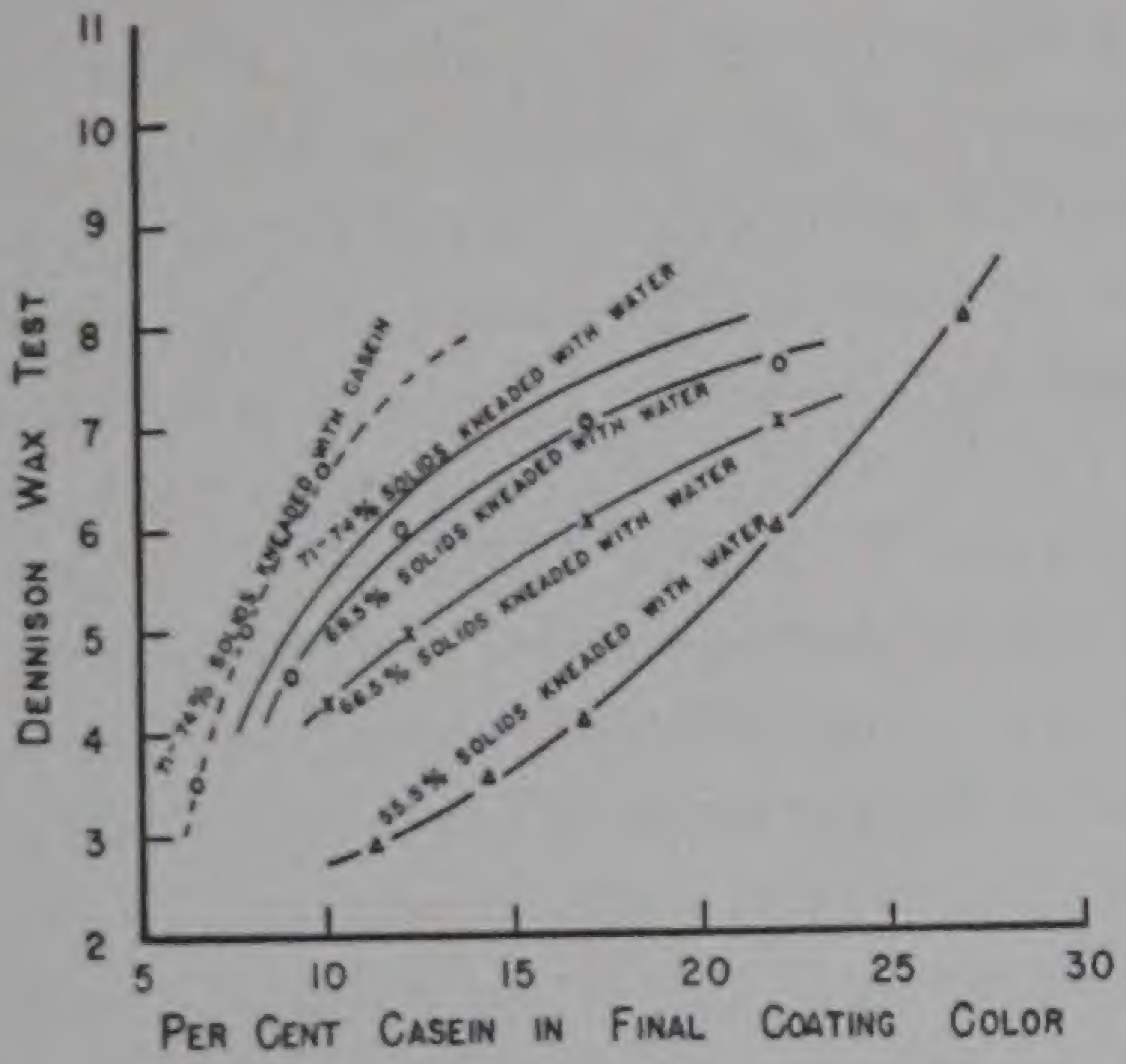

Fig. XVIII-17. Effect of kneading precipitated calcium carbonate slurries for 45 minutes at different solids content in the presence of water and casein[103] (courtesy Wyandotte Chemicals Corp.).

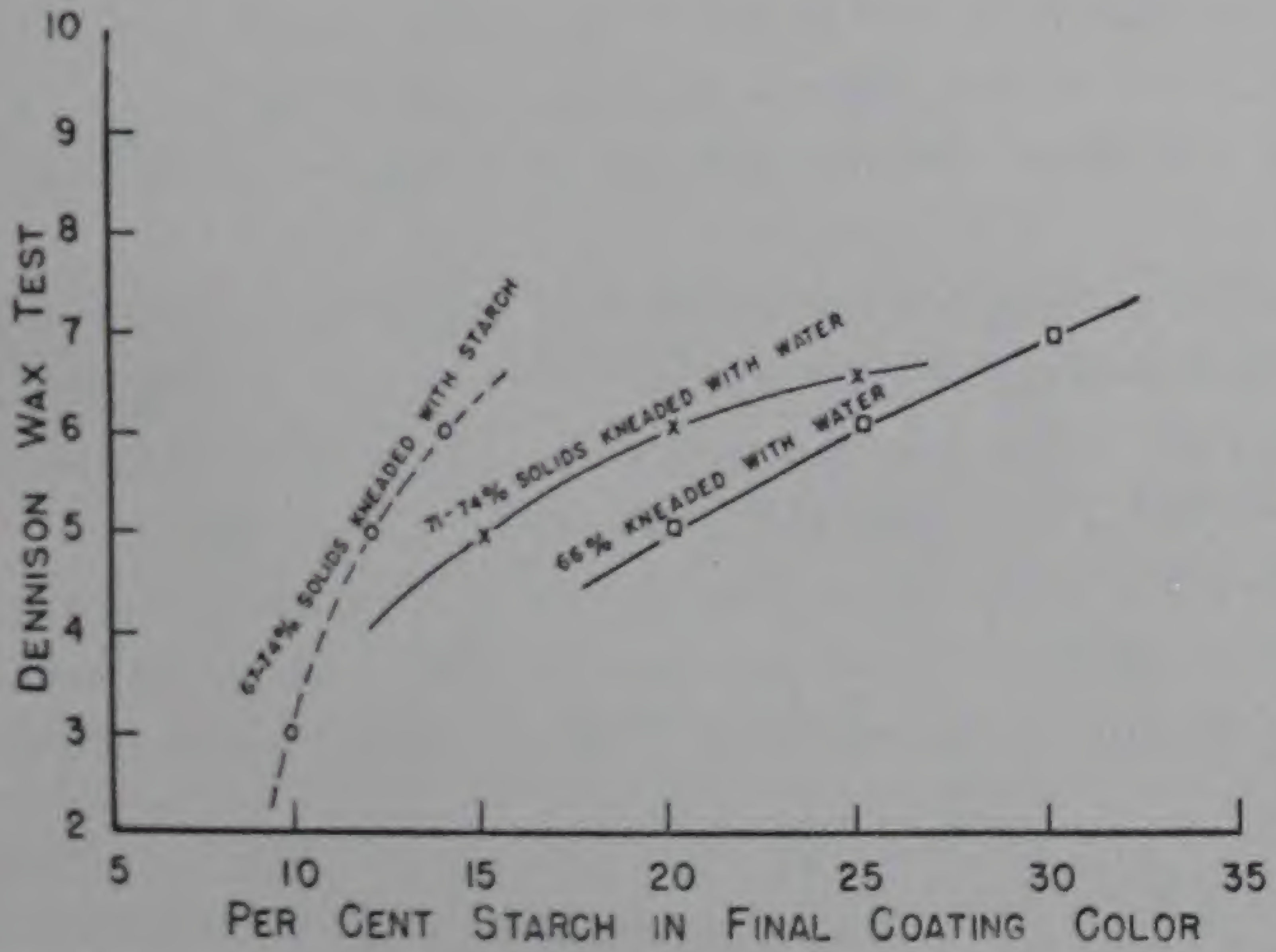

Fig. XVIII-18. Effect of kneading precipitated calcium carbonate slurries for 45 minutes at different solids content in the presence of water and starch[103] (courtesy Wyandotte Chemicals Corp.).

One interesting development has been the use of special dispersion equipment such as colloid mills, rod mills, and kneaders for reducing the adhesive demand of precipitated calcium carbonate. For many years, excessive adhesive demand was a deterrent to the use of precipitated calcium carbonate in paper coating, but recent developments in dispersion methods have reduced the adhesive demand by about 10 to 25%, depending upon the grade of carbonate used. Roderick[102,103] describes two methods of handling: (*1*) the pigment and total amount of adhesive may be kneaded or milled in a plastic condition and then diluted with water, or (*2*) the pigment and a small amount of adhesive may be kneaded while plastic and then the remaining adhesive and water added. Either method brings about a tremendous reduction in the adhesive demand of the pigment, but the extent of the reduction in adhesive demand depends upon the type of dispersing equipment and the solids content of the pigment slurry. With kneading equipment such as dough mixers or pony mixers, slurries up to 70 to 75% solids can be used; if ball milling is used, slurries up to 50 to 70% solids can be used.[103] Figure XVIII-17 and Figure XVIII-18 show the reduction in adhesive demand which is obtained with casein and starch adhesives respectively, using different methods of kneading compared with the regular method of dispersion with blade type mixers.[103] Wilson[104] has patented a method of grinding aqueous suspensions of calcium carbonate with a deflocculating agent to reduce the adhesive requirement of the pigment. Treatment of calcium carbonate adhesive mixtures in the above ways brings about a more intimate mixture of the pigment and adhesive. The effect is due to a breaking down of the agglomerated highly porous calcium carbonate particles, which releases the adhesive held in the capillary pores so that it is free to act to its fullest extent as a bonding agent. As a result, more of the adhesive is made available to function as a bonding agent, with the effect that the strength and density of the final coating are increased.

Before the coating mixture is used, it should be screened to remove any dirt particles, undispersed pigment particles, lumps of adhesive, and similar coarse material. The grit retained on a 100-mesh screen should be less than 0.1 to 0.2% in a properly prepared coating mixture. In machine coating, there is a tendency in some cases for the coating mixture to pick up "lint" or paper fibers and, for best results, these should be removed before the coating mixture is recirculated. Self-cleaning screens are desirable for this purpose.

Coating Formulas

The two major ingredients of the coating formula are the adhesive and the pigment. The relative proportion of these can be varied, depending upon the results desired, but in general, the pigment comprises from 75 to 90% by weight of the dry ingredients, and the adhesive comprises from 10 to 25%. The water content generally ranges from 70 to 30%, and con-

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[102] H. F. Roderick, *Paper Mill News* 68, No. 26: 17–19 (June 30, 1945)

[103] Bulletin, "Adhesive Savings with Wyandotte Precipitated Calcium Carbonate," Wyandotte Chemicals Corporation, Wyandotte, Michigan

[104] A. D. Wilson, U. S. 2,343,243 (Apr. 11, 1944)

versely, the solids content ranges from 30 to 70%. Table IX shows several typical coating mixtures.

TABLE IX

TYPICAL COATING FORMULAS

Grade of coated paper	Pigment composition	Dispersing and other agent	Adhesive	Per cent solids
Brush-coated book paper	100 parts clay	0.3 part sodium hexametaphosphate 0.2 part soap	20 parts oxidized starch	45
Brush-coated magazine paper	80 parts clay 20 parts calcium carbonate	0.3 part sodium hexametaphosphate 0.2 part soap	25 parts enzyme converted starch	42
Brush-coated magazine paper	75 parts clay 25 parts satin white	0.3 part sodium hexametaphosphate	18 parts alpha protein	38
Brush-coated folding enamel	80 parts clay 20 parts calcium carbonate	0.1 part sodium pyrophosphate	15 parts casein	45
Machine-coated book paper	100 parts clay	0.2 part sodium hexametaphosphate 0.2 part soap	15 parts dextrinized starch	55

Many coating formulas are made with pigment blends in order to combine the desirable properties of two or more pigments. For example, clay and calcium carbonate may be used together in order to derive a high finish from the clay and a high brightness from the carbonate. Clay-satin white and clay-titanium dioxide are other typical combinations. On the other hand, adhesives are seldom blended, with the exception of latex which is widely used with casein and in some cases with starch.

Commercial coating formulas usually contain a number of minor ingredients, in addition to the adhesive and pigment. These materials are not an essential part of the coating mixture, but are added for special effects. Among the materials which may be added are the following: eveners, antifoaming agents, wetting agents, dyestuffs, and pigment-dispersing agents. These include such materials as pine oil, sulfonated oils, soaps, wax emulsions, and resin emuslions.

Pine oil and sulfonated oils (e.g., sulfonated castor oil and sulfonated tall oil) are sometimes added to the coating mixture, usually in proportion of 0.1 to 0.5% on the total volume of coating mixture. The principal function of these agents is to aid in smoothing of the coating and to prevent the formation of pinholes. Pine oil also has a definite preserving action, and is widely used in wallpaper coating for this purpose. Another function of these ingredients is to improve the flexibility of the coating, especially during the winter months. Too high a percentage of these materials must be avoided, however, since they lead to the formation of oil spots in the coating. Getty[105] found that coating mixtures can stand much higher percentages of sulfonated tall oil compared with other sulfonated oils without showing oil spots or other bad effects.

Anti-foaming agents are frequently added to the coating mixture, and the use of these agents will be discussed later in this chapter. Softening agents, such as invert sugar, glycerine, or corn syrup, may be used on occasion to increase the pliability of the coating, but the use of these materials is not general.

Wax emulsions and soluble soaps (ammonium stearate and sodium oleate) are frequently added to starch coatings to reduce dusting during calendering (by increasing the pliability of the coating) and to improve the leveling properties of the coating. Wax emulsions are frequently used in casein coatings for the production of friction-glazed papers. Soluble soaps should be added as the last ingredient after the coating mixture has been lowered to room temperature. Insoluble soaps (e.g., calcium stearate) may be added to improve the brightness and gloss of the coating and to prevent too rapid absorption of ink when the paper is printed. Glyceryl tristearate is another material sometimes used in paper coatings. However, all these materials must be used with caution, because excessive amounts detract from the properties of the coating and cause trouble with poor drying of printing inks. In roll coating, the rubber-covered offset roll sometimes undergoes more rapid deterioration when these ingredients are used in the coating formula.

Shellac is sometimes used in paper coating formulas where water resistance is desired. The shellac is usually dispersed with ammonia in the following proportions before being added to the coating mixture: 50 lb. shellac, 2–3 qt. ammonia (26° Bé.), 50 gal. water.

Soluble dyestuffs are sometimes added to produce colored coatings. Dyestuffs are used for tinting when off shades of white are desired, red and blue dyestuffs being the most widely used. If colored pigments are used in the coating, dyestuffs may be added to tone up or increase the brilliance of the coating. The precautions to be observed in the use of soluble dyestuffs in coating are the same as those in other dyeing operations. The dyestuff should always be dissolved in water before adding to the coating mixture. Acid dyestuffs are generally used because of their brilliance and fastness to light and heat. Basic dyes are extremely brilliant, but most of them are too fugitive to light, alkali, and moist heat to be used in the preparation of colored coatings. Direct dyes tend to produce dull coatings.

Per Cent Solids

The per cent of solid matter in the coating mixture has become a matter of increasing importance since the introduction of machine coating.

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[105] E. Getty, *Paper Trade J. 114,* No. 8: 95–96 (Feb. 19, 1942)

High-solids coating mixtures are desirable because they permit higher machine speeds. Dickerman and Riley[106] report that a solids content of 53% permits a machine speed of 930 f.p.m., compared with only 750 f.p.m. for a coating mixture of 45% solids. The higher operating speeds obtainable with coating mixtures of high solids is readily understood when it is realized that a coating mixture of 40% solids requires the evaporation of about 1.5 lb. of water per ream of paper for each pound of dry coating applied, whereas less than 0.5 lb. of water need be evaporated for a coating mixture of 70% solids.

It is customary in coating terminology to divide coatings into high-solids coating mixtures and low-solids coating mixtures. These terms are quite flexible, but in general, cover the range of 30 to 50% solids for low-solids coating mixtures and 50 to 70% solids for high-solids coating mixtures.

A high-solids coating mixture may be obtained by one of two methods. In the first method, the coating formula can be the same as that used in low-solids coating, except that part of the water is withheld. This produces a coating mixture of very high viscosity, and if carried far enough, produces a mixture of putty-like consistency. Such a coating mixture has only a limited use, and while it can be applied by certain high-speed roll coaters, it cannot be handled by many conventional coating machines. Increasing the solids content of a coating mixture in this way not only increases the viscosity, but also increases the plasticity of the coating mixture. The second method of obtaining a high-solids coating is based upon special formulas containing low-viscosity adhesives so that even though the solids are high, the coating mixture is fluid and workable. The flow properties of this type of coating mixture are governed by the viscosity of the adhesive and, to a lesser extent, by the flow properties of the pigment.

The most important factor determining the practical range of solids content is the viscosity of the adhesive. Casein has a relatively high viscosity in the native state but by suitable techniques it can be used in coating mixtures at 60 to 63% solids. Starch also has an extremely high viscosity in the native state and, if used as such, would necessitate a coating mixture of very low solids. However, starches are generally used in modified form (i.e., after conversion by enzymes, oxidizing agents, or dextrinizing agents) so that their viscosity is greatly reduced. If a low viscosity starch is used, coating mixtures up to 70% solids and even higher can be produced.

Another important factor determining the optimum solids content of the coating mixture is the type of pigment used. Pigments requiring only a small amount of water to produce a fluid dispersion are particularly useful for preparing high-solids coating mixtures for machine coating. Water-ground calcium carbonate produces a dispersion of higher fluidity than precipitated calcium carbonate, but it cannot be used in machine (roll) coating because it fractionates out at the nip. Satin white requires a high ratio of water to pigment to produce a fluid dispersion. Certain types of clay produce more fluid dispersions than other clays. Clays of small particle size and low hydration capacity produce more fluid dispersions than clays of large particle size and high hydration capacity.[107] An important factor in calculating solids content is the moisture content of the pigment, since a change in moisture content from 6 to 10% can cause a variation of nearly 3% in solids content in high-solids coating mixtures.[108]

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[106] G. K. Dickerman and R. W. Riley, U. S. 2,425,231 (Aug. 5, 1947)

The optimum solids content of a coating mixture is determined in part by the type of coating process used, because certain coaters can handle more viscous coating mixtures than others. Each coating process has certain requirements in the matter of viscosity, yield point, and other rheological properties of the coating mixture which cannot be exceeded without running into operating difficulties. For example, coating mixtures for brushtype coaters must have a low viscosity and a low plasticity in order to spread easily on the surface of the paper by brushing. In order to attain these properties, the solids content of the coating mixture must be relatively low, usually in the neighborhood of 30 to 40%; if the solids content is much greater than this, the coating is likely to show brush marks. Air brush coaters and centrifugal spray coaters also require coating mixtures of relatively low solids, usually 38 to 45%, although coating mixtures up to 60% solids can be handled when low-viscosity starches are used as the adhesive. Roll coaters can handle coating mixtures of much higher solids, because they can handle coating mixtures of much higher viscosity. The ability of roll coaters to handle coating mixtures up to 60 to 70% solids accounts for the wide use of roll coaters in machine coating where high solids are desirable to reduce the drying load on the machine. The usual solids for a coating mixture for knife coating is 45 to 47%. Machine-coated papers must dry rapidly so that the coating will not be scratched by the drier surface.

In addition to increased machine speed, there are other advantages to operating at high solids. For example, the strength of the dried coating is generally improved as the per cent solids is increased, more so with starch than with casein, and more so with certain types of starch than with others. The effect of increasing solids content on the strength of the coating as measured by the Dennison wax number is shown in Table X. The same ratio of starch to pigment was used, and the same amount of dry coating

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[107] K. A. Arnold, *Paper Trade J. 117*, No. 9: 98–104 (Aug. 26, 1943)
[108] I. L. Lester and S. C. Lyons, *Paper Trade J. 125*, No. 17: 189–195 (Oct. 23, 1947)

TABLE X

EFFECT OF SOLIDS CONTENT OF COATING MIXTURE ON STRENGTH OF COATING

Solids content of coating mixture, %	Dennison wax number
40	3.5
50	4.0
60	4.5
70	5.5

was applied to the paper in all cases, but the per cent solids of the coating mixture was varied.

Flow Properties of Coating Mixtures

Rheology (flow) is a subject of great interest to the coating chemist, particularly in the machine coating field. The rheological properties of coating mixtures for machine coating determine the amount of coating which will be applied to the paper under a given set of conditions, and also determine the leveling out properties of the coating after application. Unless the coating mixture has the proper flow properties, improper transfer will result and weird patterns will be produced.

Before discussing the flow properties of coating mixtures, it is desirable to discuss briefly the subject of flow in general. Flow occurs in a liquid as the result of applied force. Viscosity is the resistance of a fluid to flow when subjected to a deforming force. If the velocity gradient is considered as taking place between parallel planes within the fluid, then velocity becomes the rate of shear at a given shearing stress. The unit measure of viscosity is the poise. A liquid has a viscosity of 1 poise when a force of 1 dyne exerted longitudinally will move a 1 cm. square plane 1 cm. per second in reference to a second plane 1 cm. away. There are four basic types of flow: Newtonian, plastic, pseudoplastic, and dilatant, as shown in Figure XVIII-19.

Newtonian (viscous) flow is the simplest type of flow. A material exhibiting viscous flow starts to flow as soon as force is applied, and the rate of flow increases in direct proportion to the applied force. If a truly viscous fluid is forced through a capillary tube (e.g., Ostwald viscometer) at different pressures, the volume of flow will be directly proportional to the applied pressure gradient. The curve obtained by plotting rate of flow versus pressure is a straight line passing through the origin, and the slope of the curve is inversely proportional to the viscosity (see Fig. XVIII-19). Thus, viscous flow is represented by the relationship discovered empirically by Poiseuille:

$$V = kP$$

where V is the volume of flow, P is the shearing stress, and k is a constant.

Because the consistency curve (plot of rate of shear versus stress for equal time intervals) for a Newtonian liquid is a straight line passing through the origin, the liquid can be defined rheologically by a single value, the coefficient of viscosity. The coefficient of viscosity is proportional to the cotangent of the angle made by the consistency curve and the stress axis and is numerically equal to the number of dynes required to induce a unit rate of shear. In viscous flow, viscosity is independent of rate of shear up to the point of turbulence.

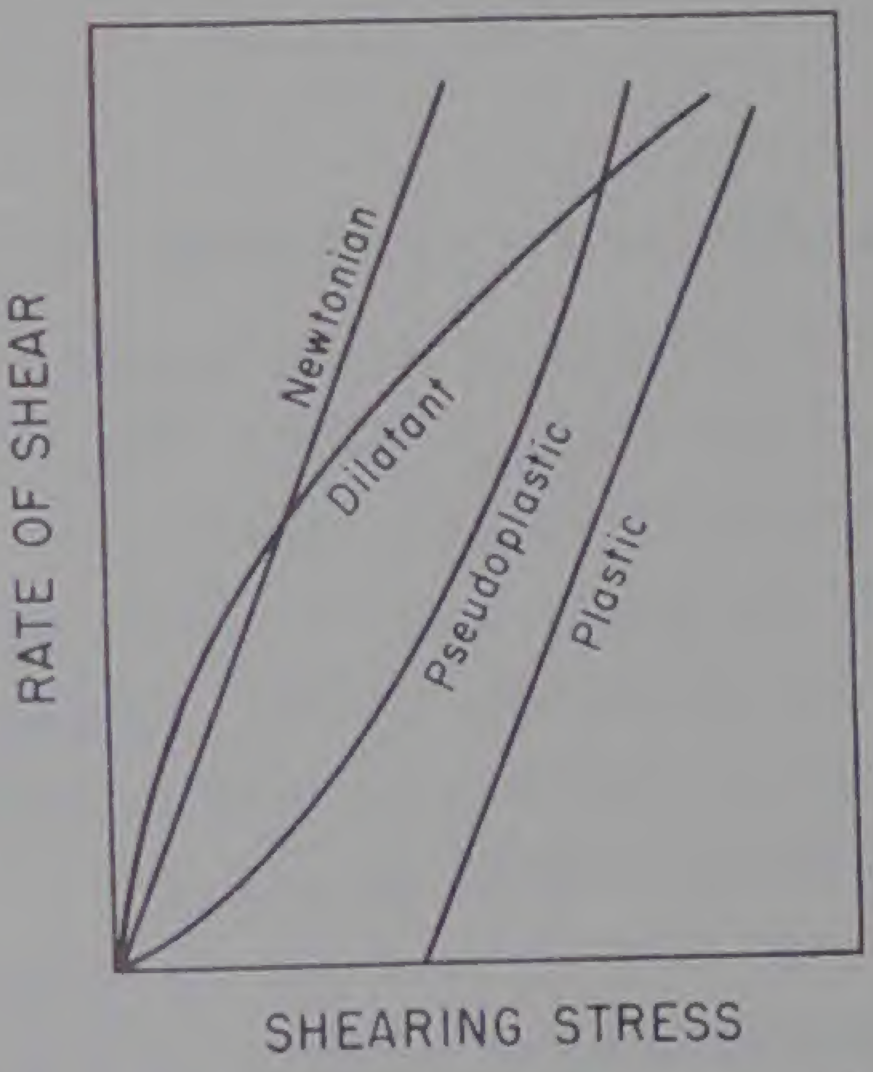

Fig. XVIII-19. Four basic types of flow.

Plastic flow is exhibited by liquids which do not flow until a certain definite minimum force, called the yield value, has been exceeded (see Fig. XVIII-19). Plastic flow is represented by the following relationship (if the flow is viscous after the yield point has been exceeded):

$$V = y + kP$$

where y is the yield value.

The resistance to flow after the yield value has been exceeded is called plastic viscosity and is represented by the slope of the curve. Plastic viscosity is thus the shearing force required to induce a unit rate of shear in excess of the yield value. At least two points are required to define the consistency curve of a plastic material, the yield point and another point to determine the plastic viscosity. Yield value cannot be properly measured in viscometers at low rates of shear because of "plug" flow, i.e., flow by which the material moves as a solid plug lubricated with a thin layer of fluid at the surface where the shearing stress is applied. A high yield value results in a property known as "shortness," that is, the inability of the material to flow under its own weight. It is quite possible for a given material to have a high yield value while the plasticity is low, and vice versa; for example, mineral oil may have a high viscosity, but no yield value, whereas a clay slip may have a low viscosity, but a high yield value. High yield value in the case of a coating mixture results in a mixture which is difficult to handle in the return lines and which has poor leveling properties on the paper. Most coating mixtures exhibit a yield point, although if the yield value is low, it may not be apparent except by measurement with a suitable viscometer. All plastic suspensions are flocculated and have an internal structure which must be overcome before flow will take place.[109] It is this initial force necessary to break down the flocculated structure which is responsible for the yield value.

In both viscous and plastic flow, the consistency curve is a straight line. However, in two types of flow the consistency curve is not a straight line, and these are known as pseudoplastic flow and dilatant flow. In pseudoplastic flow, the consistency curve bends away from the stress axis at high rates of shear, but the curve extrapolates to the origin and thus resembles Newtonian flow at low rates rates of shear in that there is no real yield value (see Fig. XVIII-19). Pseudoplastic flow is attributed to internal structure which is broken down by increasing rates of shear, thus reducing the frictional resistance. As a result, rate of shear increases faster than linearly with an increase in shearing stress. As a general rule, time has no influence on the rate of breakdown, that is, the rate of shear at a given shearing stress is the same for increasing as it is for decreasing stress, although there may be a slight hysteresis effect at very high rates of shear.[110]

Dilatancy is the opposite of pseudoplasticity in that the consistency curve bends toward the stress axis (see Fig. XVIII-19). In other words, increasing the shearing force produces a smaller increase in rate of shear than expected. Dilatancy is a condition of minimum voids. In a dilatant system, the dispersed particles and the liquid are in such close balance that there is barely enough liquid to fill the voids. When flow is initiated, the void volume is slightly increased, thereby creating a partial dryness which increases the resistance to flow. Thus, dilatancy is found only in highly concentrated, deflocculated dispersions, since flocculation prevents dilatancy by making it impossible for the particles to assume a position of minimum voids.

An extremely important flow characteristic in coating mixtures is thixotropy. Thixotropy is somewhat the same as pseudoplasticity in that an increase in shearing stress produces a larger increase in rate of shear than expected, but there is the important difference that thixotropic changes are affected by time, whereas pseudoplastic changes are produced instantaneously. Thixotropy is believed to be due to an internal structure which imparts rigidity to the system. This structure is broken down and a viscosity equilibrium is reached if the system is agitated for a period of time at constant rate of shear. However, once the shearing stress is removed, the structure responsible for thixotropy reforms and the system returns to its original state, but a significant time interval is required for this to take place. Thixotropy is difficult to measure, and the usual criterion of measurement is the hysteresis loop which is produced by the up- and downcurves of the consistency diagram. A loop is produced because the upcurve bends away from the horizontal or stress axis, whereas the downcurve is essentially straight, except at the lower end (see Fig. XVIII-20). Thixotropic behavior can be superimposed on any of the other basic types of flow.

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[109] H. Green, *J. Applied Phys. 13,* No. 10: 611–622 (Oct., 1942)

[110] R. N. Weltmann, *Ind. Eng. Chem., Anal. Ed. 15:* 424–429 (July 15, 1943)

Single-point flow measurements are satisfactory for defining the flow properties of Newtonian liquids, but multipoint consistency curves obtained under known conditions are required in the case of non-Newtonians. This is necessary since a single reading taken at one particular rate of shear is not sufficient to define the shape of the curve for non-Newtonians. Even three or four points are often inadequate for non-Newtonians, since these often fail to disclose the complex nature of the curve as, for example, when thixotropy and dilatancy exist in the same system. Because nearly all coating mixtures are non-Newtonians, viscosity measurements made with a standard orifice or pipette type viscometer having a fixed rate of shear are of little or no value as a guide to the flow characteristics for high-speed roll coating. Hence, special viscometers are required in coating technology to measure the flow at different rates of shear. The most suitable types are rotational type viscometers which, in general, subject the material to a known shearing rate and measure the resulting shearing stress. The most common of the rotational viscometers are the Stormer, MacMichael, Brookfield, and Hercules Hi-Shear. The Stormer, Brookfield and Hercules viscometers consist of a cylinder or bob which rotates in a stationary cup, whereas the MacMichael viscometer consists of a cup which rotates and a cylinder which is stationary.

In the MacMichael viscometer, a metal disk is suspended by a fine torsion wire and a cup in which the disk is rotated at a definite, but variable, r.p.m. When the cup is filled with the liquid to be tested and driven by the motor, the resisting force of the liquid is measured by the angle or torque through which the torsion wire is twisted. The number of degrees by which the wire is twisted is measured on a scale graduated from 0 to 360°. The degrees twist represents the applied stress, and the speed of the cup represents the rate of flow or rate of shear. When the degrees torque is plotted against r.p.m., a straight line is obtained if the coating mixture is truly viscous. A viscosity figure can be obtained from such a curve by taking the slope of the line, or the viscosity can be measured as the degrees MacMichael at some arbitrarily selected r.p.m., e.g., 56 r.p.m. The fluidity, which is the reverse of the viscosity, is obtained by dividing the degrees twist by the r.p.m., usually at 56 r.p.m. If the coating mixture is not truly viscous, plasticity will be evident, and this can be measured by extrapolating the curve to the point where it intercepts the vertical axis. The value, at zero r.p.m., is taken as the yield point. The mobility (which is equivalent to the fluidity in a truly viscous dispersion) is measured by subtracting the yield point from the degrees twist and dividing by the r.p.m. in order to obtain the slope of the curve. The shape of the curve indicates the type of flow. For example, a straight line represents either plastic or viscous flow; a line curving downward toward the horizontal (r.p.m.) axis represents pseudoplastic flow; a line curving away from the horizontal (r.p.m.) axis represents dilatant flow.

A method of measuring thixotropy on the MacMichael viscometer is illustrated in Figure XVIII-20.[110a] The degrees twist are plotted against r.p.m. for both increasing and decreasing speed settings. At increasing speeds, a typical curve bending toward the r.p.m. axis is obtained, whereas at decreasing speeds, a straight line is obtained. The area between the two curves is a measure of the thixotropic breakdown. The slope of the downcurve in Figure XVIII-20 is a function of plastic viscosity, and the intercept of this line with the vertical axis is a function of yield value.

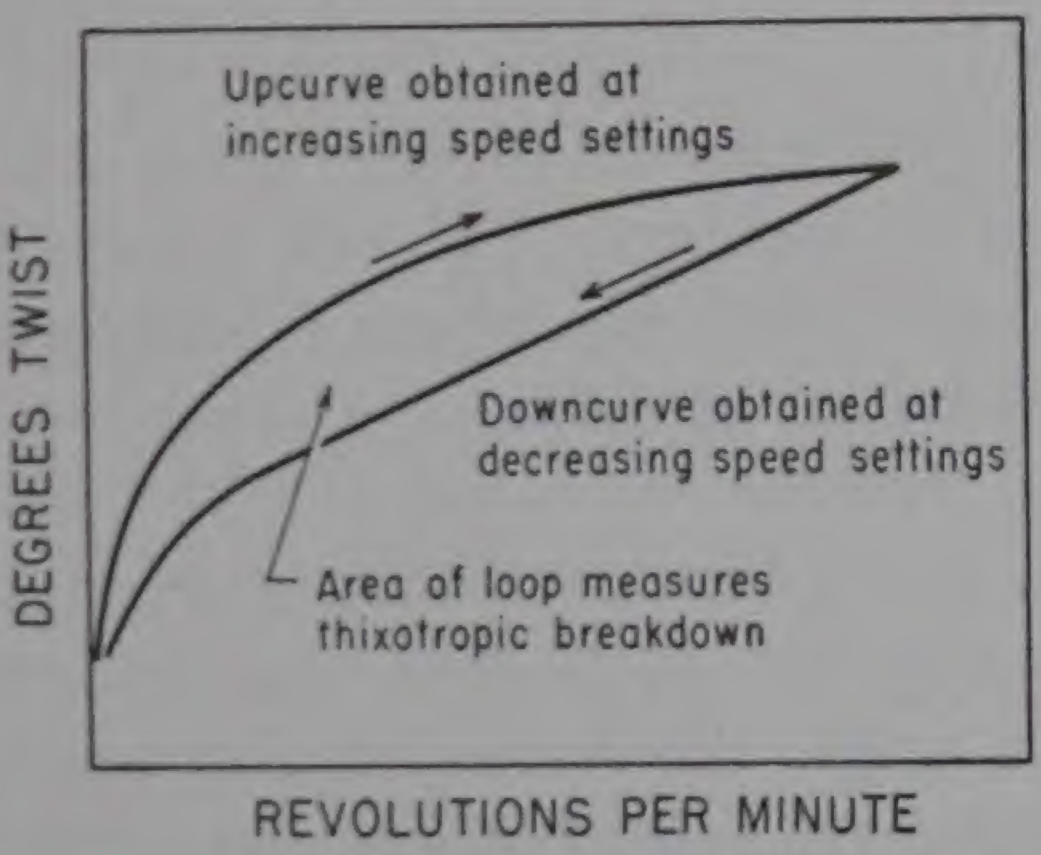

Fig. XVIII-20. Thixotropy as indicated by MacMichael viscometer.

Still another method of measuring thixotropy is by subjecting the coating mixture to a high rate of shear for an appreciable period of time, reducing the rate of shear to a lower value, and then recording the build-up in viscosity with time.

The Brookfield synchrolectric viscometer is another widely used instrument. This instrument consists of a spindle which is rotated by means of a small synchronous rotator through a special, calibrated spiral spring which measures the viscous drag on a calibrated dial. Viscosity readings can be made at different speeds. Viscosity (in centipoises) can be plotted against rates of shear (rate of spindle rotation), and a flow curve thus obtained.

[110a] S. Hoaglund, "The Rheology of Surface Coatings," R–B–H Dispersions, Inc. (1946)

The rates of shear obtained in the nip of high-speed coating rolls are much greater than those obtained in the rotational viscometers described above. Thus, it is possible that different flow behavior occurs during coating than is indicated by MacMichael, Brookfield, or Stormer viscometer readings. Special high-shear viscometers have been developed which are capable of developing shearing forces more nearly within the range developed in high-speed coating processes.[111, 112] One of the most interesting of these is the Hercules Hi-Shear viscometer which produces a rheogram or plot of rate of shear versus shearing stress for equal time intervals. This instrument consists of two concentric cylinders, a cup and a bob, which fit very close tolerances. In operation, the cup is filled with coating mixture, and the bob is lowered into the liquid. The bob can be rotated at speeds up to 1,050 r.p.m., which develops rates of shear about 200 to 700 times greater than the conventional viscometers. The cup rotates by the torque transmitted through the liquid, and this torque is measured in terms of linear deflection of a calibrated set of springs. Curves are obtained by turning the control handle so that the top speed (1,050 r.p.m.) is reached in the desired time interval, after which the handle is reversed back to zero speed. Two curves, the upcurve and downcurve, are obtained. These are automatically plotted on a graph, the vertical axis of which gives rate of shear in r.p.m., and the horizontal axis of which gives shearing stress (torque) in dyne-centimeters × 10^5. If the material tested is truly viscous, the two curves coincide and pass through the axis. If the material is thixotropic, the upcurve bends toward the vertical axis, whereas the downcurve is linear. If the material is dilatant, the upcurve bends toward the horizontal axis. The yield point is determined by projecting the downcurve in a straight line to the horizontal axis to determine the yield stress in dyne-centimeters. By taking readings on the upcurve at two different speeds (usually 500 and 1,000 r.p.m.), it is possible to calculate apparent viscosity (n), plastic viscosity (u), yield stress (F), rate of shear coefficient of thixotropy (M) and leveling index (L.I.). The leveling index, which is a dimensionless ratio of the coefficient of shear thixotropy to the plastic viscosity, is an important measure of the suitability of coating mixtures for high-shear roll coating, since it indicates the ease with which the coating will level after leaving the nip. A high leveling index is obtained if the coating mixture has a high degree of thixotropy and low plastic viscosity. Normally, the leveling index does not change with the solids content of the coating mixture, which indicates that it represents the amount of thixotropy per unit of

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[111] H. Green, *Ind. Eng. Chem., Anal. Ed. 14*, No. 7: 576–585 (July 15, 1942)

[112] J. W. Smith and P. D. Applegate, *Paper Trade J. 126*, No. 23: 60–66 (June 3, 1948)

plastic viscosity inherent in the coating formulation.[113] Values for leveling index less than 0.20 to 0.25 are considered unsatisfactory, whereas values over 0.35 indicate good performance. A typical curve obtained on the Hercules Hi-Shear viscometer using a bob 2.5 cm. in height is shown in Figure XVIII-21. Calculations are shown below.

Instrument constants are required for calculating yield value and plastic viscosity. A constant for all rotational viscometers is 9.55, but S and C are instrument constants for the particular bob employed. In the particular example below, the bob constant $S = 3.758 \times 10^{-4}$ and $C = 0.01634$:

Torque at 1,000 r.p.m. (from curve) $T_{1000} = 448{,}000$ dyne-cm.
Torque at 500 r.p.m. (from curve) $T_{500} = 309{,}000$ dyne-cm.
Torque axis intercept of extrapolated straight line portion of downcurve (from curve) $T_2 = 91{,}000$ dyne-centimeters.

Apparent viscosity at 500 r.p.m. $N_{500} = \frac{9.55 T_{500} S}{\text{r.p.m.}} =$

$$\frac{9.55 \times 309{,}000 \times 3.758 \times 10^{-4}}{500} = 2.22 \text{ poises.}$$

Plastic viscosity at 1,000 r.p.m. $U_{1000} = \frac{9.55(T_{1000} - T_2)S}{\text{r.p.m.}} =$

$$\frac{9.55(448{,}000 - 91{,}000) \times 3.758 \times 10^{-4}}{1000} = 1.28 \text{ poises.}$$

Plastic viscosity at 500 r.p.m. $U_{500} = \frac{9.55(T_{500} - T_2)S}{\text{r.p.m.}} =$

$$\frac{9.55(309{,}000 - 91{,}000) \times 3.758 \times 10^{-4}}{500} = 1.56 \text{ poises.}$$

Yield stress $F = T_2 C = 91{,}000 \times 0.01634 = 1487$ g./sq.cm.
Rate of shear coefficient of thixotropy $M = 2(U_1 - U_2)/\ln(\omega_2^2/\omega_1^2)$

$$\frac{2(1.56 - 1.28)}{2 \times 2.3 \times \log_{10} 2} = \frac{0.28}{0.69} = 0.406 \text{ dyne/cm.-sec.}$$

Leveling index $\quad \text{L.I.} = \frac{M}{U_{1000}} = \frac{0.406}{1.28} = 0.32.$

Arnold[114] suggested a method of measuring flow behavior which is in close agreement with the effects obtained on commercial roll coaters. This method is based upon the use of a heavy metal roll which travels down an inclined plane at high speed and passes over a small quantity of coating mixture placed on a sample of paper on the inclined plane. The area over which the coating is spread by the action of the roll is an indication of the flow. A fluid coating mixture will be spread over a greater area than a viscous coating mixture, and a thixotropic mixture will spread over a greater area than a dilatant mixture.

The correct rheological properties depend primarily upon the type of coating process in which the coating mixture is to be used. Brush coating is best carried out with coating mixtures exhibiting Newtonian or slightly dilatant flow. According to the results in one mill, coating mixtures for brush coating must have a MacMichael viscosity between 25 to 35, and a yield point below 10, and preferably below 5. These results are based on values obtained with the MacMichael viscometer at 25° C., using the disk type plunger and a No. 26 torsion wire. If the yield point is over 10, brush marks will be visible in the coated paper.

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[113] J. W. Smith, R. T. Trelfa and H. O. Ware, *Tappi 33,* No. 5: 212–218 (May, 1950)

[114] K. A. Arnold, *Paper Trade J. 117,* No. 9: 98–104 (Aug. 26, 1943)

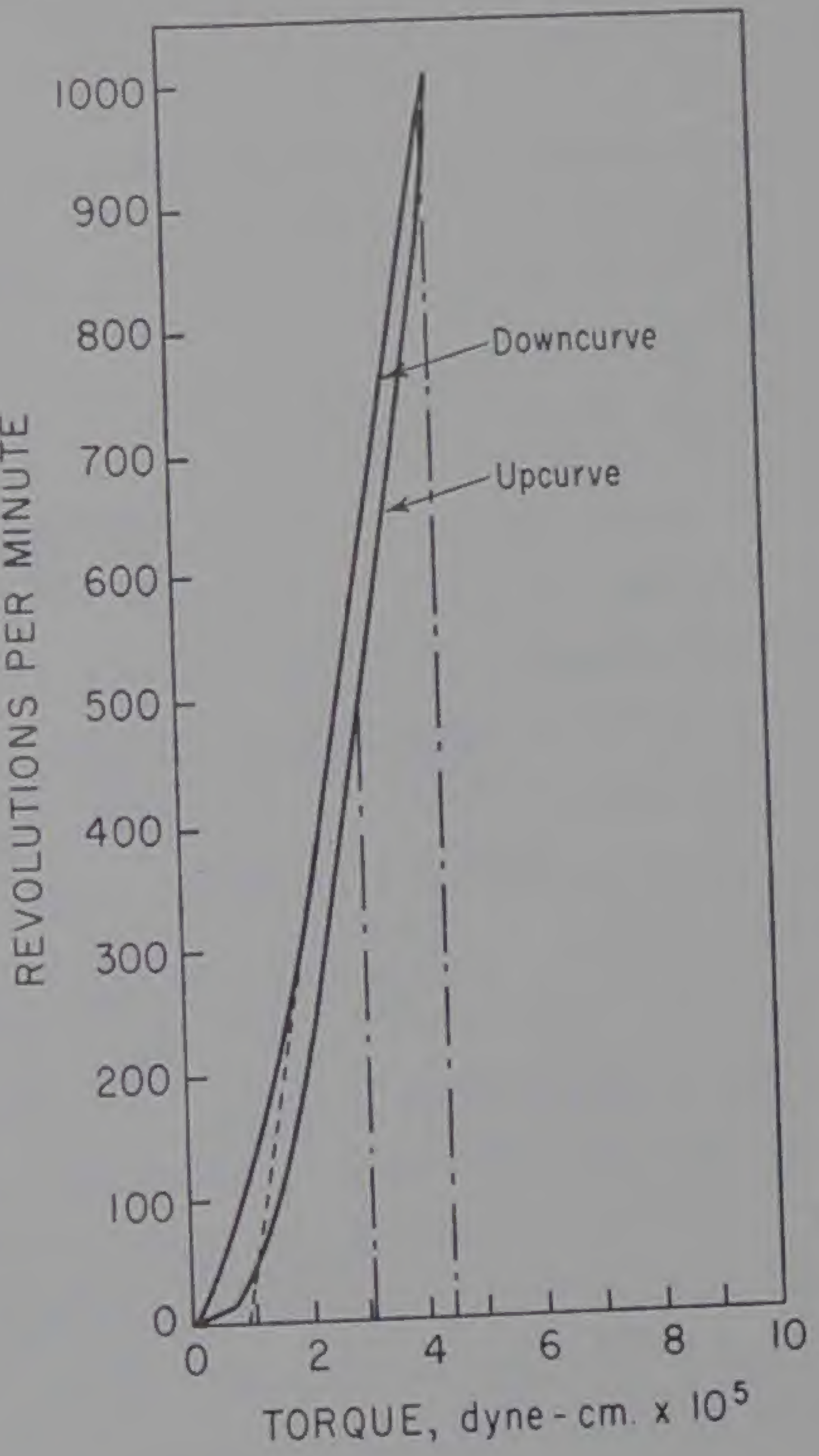

Fig. XVIII-21. Consistency diagram of coating mixture obtained on Hercules Hi-Shear viscometer.

Coating mixtures for machine or roll coating may have a higher yield point and greater palsticity than coating mixtures for brush coating. A certain degree of thixotropy is desirable when heavy-bodied coating mixtures are used for high-speed roll coating, since thixotropy permits the coating mixture to become more fluid under the shearing action of the coating roll, thus permitting the coating to flow out and produce a level surface. Excessive penetration of the coating into the raw stock is eliminated by the rethickening which occurs after the shearing stress is removed. In certain cases, a dilatant coating mixture may be desirable in order to inhibit excessive penetration of the coating into the raw stock at the time of its application to the paper, but ordinarily, coating mixtures having a marked dilatant character tend to produce coatings which are rough and mottled, due to a piled effect on the surface. As mentioned above, the leveling properties of coating mixtures for high-speed roll coating are best measured by a high-speed rotational instrument such as the Hercules Hi-shear viscometer. The importance of the correct flow properties in obtaining proper leveling of the coating on the paper is discussed later in the section on smoothing the coating.

A large number of variables affect the flow properties of the coating mixture at the time of application to the paper. Rowland[115] lists the following: clay mineral species, particle size of clay, base exchange of clay, absorptive qualities of raw stock, solids content of coating mixture, amount and type of adhesive, amount and type of mineral dispersing agent, pressure of coating rolls, and speed of machine.

The relationship which exists between the per cent solids and the flow behavior have been discussed in the preceding section. This is an important relationship, inasmuch as increasing the concentration of either the pigment or the adhesive in the coating mixture increases not only the viscosity, but also the yield point and the tendency toward anomalous flow. The effect of solids content on the flow properties is different for different coating mixtures.

The optimum flow properties of the coating mixtures are related to the absorbency of the coating raw stock. Dickerman and Riley[116] list the following requirements for coating mixtures to be used on absorbent and non-absorbent papers. The Stormer viscometer, with a 500-g. load on the driving pulley and a temperature of 40° C., was used for measuring flow properties. The viscosity is reported in seconds for 100 revolutions of the rotor.

Sheet type	Viscosity, sec.	Yield value dynes/sq.cm.	Mobility, rhe
Absorbent	150	5130	0.09
Non-absorbent	6	600	0.28

The particle size and particle size distribution of the pigment has an important influence on the flow properties of the coating mixture. As a general rule, the finer clays tend to produce the more viscous coating mixtures. Clays containing a high percentage of large particles (i.e., 8–10 microns) tend to produce dilatant coating mixtures, whereas clays having a high percentage of small particles (0.8–1.0 micron or lower) tend to produce thixotropic coating mixtures. Clays of low hydration capacity tend to produce low-viscosity dilatant coating mixtures.[117] Another extremely important factor is the degree of dispersion of the pigment. If the pigment is flocculated, the coating mixture will have a higher viscosity and a higher yield point than if the pigment is well dispersed or deflocculated.

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[115] B. W. Rowland, *Paper Trade J. 112,* No. 26: 311–313 (June 26, 1941)
[116] G. K. Dickerman and R. W. Riley, U. S. 2,425,231 (Aug. 5, 1947)
[117] K. A. Arnold, *Paper Trade J. 117,* No. 9: 98–104 (Aug. 26, 1943)

Although part of the viscosity of a coating mixture must be attributed to the pigment, the adhesive is responsible for most of the body or viscosity. In general, the higher the ratio of adhesive to pigment, the higher the viscosity of the coating mixture. The coating chemist should regard the pigment and adhesive as two very active colloidal substances which are in competition for the water, dispersing agent, cations, and other minor ingredients in the coating mixture. This concept is particularly apropos for clay, which is an extremely active colloidal pigment. It is likely that a redistribution of water and ions occurs when clay and adhesive are brought into contact, and for this reason, sufficient time should be allowed after mixing to permit changes to take place and to allow the coating mixture to come to a state of equilibrium. The final effect may be quite different from that which is obtained upon the initial mixing of the ingredients.

The effect which is obtained upon the mixing of adhesive and pigment is difficult to predict. It is possible, for example, that a given adhesive will cause thickening when mixed with one clay and thinning when mixed with another clay. This may be attributed to the fact that the redistribution of exchangeable cations affects the hydration of the clay unfavorably in one case, and favorably in the other. Rowland[118] describes how starch may affect the flow characteristics of clay dispersions in either direction. Starch may produce a thickening effect by robbing the clay of dispersing agent and thereby reduce the effective concentration of dispersing agent below that necessary for maximum fluidity. On the other hand, if the clay contains an excess of dispersing agent, starch may remove enough dispersing agent to reduce the amount to that necessary for minimum viscosity. Thus, the point of maximum fluidity of the coating mixture may not always coincide with the maximum fluidity of the clay-water dispersion. By the same token, the most easily dispersed clays do not always produce the most fluid coating mixtures. As a general rule, more dispersing agent is required for minimum viscosity in a coating mixture than is required in the clay-water slip, particularly if oxidized starches are used, because of the tendency of the starch to rob the clay of dispersing agent. The use of alkali (about 0.1% sodium hydroxide on weight of clay) in combination with the dispersing agent is helpful in lowering the viscosity, particularly if starch is used as the adhesive.[119] In the case of casein coating mixtures, only the minimum amount of dispersing agent necessary for proper dispersion of the pigment should be added prior to the addition of the adhesive, since excessive dispersing agent in presence of casein causes marked thickening of clay.

[118] B. W. Rowland, *Paper Trade J. 112,* No. 26: 311–313 (June 26, 1941)
[119] W. R. Willets, *Tappi 33,* No. 4: 201–208 (Apr., 1950)

Casein and starch adhesives produce coating mixtures having different flow properties. Casein coating mixtures are normally stringy and exhibit Newtonian flow at low solids and are generally plastic and slightly dilatant at high solids. Casein coating mixtures are widely used in brush or air knife coating where low solids are permissible and viscous flow is desirable, but they are not well adapted to high-solids roll coating because of their tendency toward dilatant flow. However, suitable coating mixtures can be prepared by modifying with sodium sesquisilicate using special techniques already described. Starch coating mixtures are generally used at high solids where they produce mixtures which are short and which exhibit thixotropic flow. Because of their high-solids and thixotropic nature, starch coating mixtures are widely used for roll coating. Soaps are frequently added to starch coating mixtures to increase the thixotropic properties. About 1% ammonium stearate, or 2 to 3% Ivory Flakes, based on the starch, is generally used. This should be added while the starch is hot; if the starch has been cooled, the soap solution should be heated. Too much soap should be avoided, since this causes a reduction in the thixotropic effect.

Water Retention

Many coating chemists use a test which measures the water retention qualities of the coating mixture. This test is usually carried out by floating a small piece of unsized paper of medium weight on the surface of the coating mixture and taking the time in seconds for the liquid in the coating mixture to pass through the paper and change the color of indicator powder which has been dusted on the surface of the paper. The indicator powder may be finely ground potassium permanganate, or it may be a mixture of dyestuff and inert ingredients in the proportions of 1 part blue dyestuff, 5 parts soluble starch, and 45 parts powdered sugar. The end point is taken as the time for the first marked change to occur in the color of the indicator. The use of a reading lens helps to judge this point.

The value of the water retention test is based upon its usefulness in predicting the rate at which the coating mixture will release liquid to the base paper. If the coating mixture has an inordinately low water retention, water will leave the film of coating too rapidly, with the result that the coating layer increases in viscosity and does not have time to level off and produce a smooth surface. On the other hand, if the water retention is too high, two things may happen: (*1*) either the coating will take too long to dry, with the result that it is marred by the drier surface, or (*2*) the coating will have too much after-flow, with the result that it forms puddles. Theoretically, there is an optimum water retention for each grade of raw stock; a coating mixture with a low water retention will work better on highly sized paper than on a weakly sized sheet. High water retention is desirable in thixotropic coating mixtures for roll coating, since a high water-holding capacity tends to resist the release of water to the base paper when the coating layer is thinned by the action of the coating roll.[118]

In most cases, a high water retention goes hand in hand with a high adhesive retention and high coating strength. The test is often used as an indication of the adhesive retentive powers of the coating mixture. Coating mixtures of high adhesive retention are required when the coated paper is to be printed with gloss inks in order to retain a larger proportion of adhesive in the coating. However, strong coatings can be prepared from coating mixtures of low water retention, e.g., when polyvinyl alcohol is used as the adhesive. There appears to be a better relationship between water retention and dusting tendencies than between water retention and strength. This relationship is based on the assumption that the adhesive in a coating mixture of low water retention tends to strike into the base paper to such a degree that the layer of coating is robbed of adhesive, thereby producing a weak coating with a tendency toward dusting.

The water retention value is influenced predominantly by the viscosity of the coating mixture and the type of adhesive. Increasing the viscosity of the coating mixture and increasing the ratio of adhesive to pigment tend to increase the water retention. On an equal adhesive-to-pigment ratio, casein and polyvinyl alcohol produce coating mixtures of higher water retention than starch. When compared on the basis of equal coating strength, however, starch coating mixtures are the equal of casein in water retention because of the higher percentage of starch which is used. On the same basis, polyvinyl alcohol coatings have a very low water retention because of the low percentage of adhesive which is required.

Although the adhesive has the predominant influence on water retention, the degree of dispersion and the degree of hydration of the pigment also have an important influence. The hydrous clays, for example, tend to produce coating mixtures of higher water retention than the less hydrous clays, because they release their vehicle to the raw stock more slowly.[118] Bentonite, which is a highly hydrous clay, produces coating mixtures of very high water retention. Calcium carbonate is much less hydrous than clay, and consequently it produces a coating mixture which releases water readily to the raw stock. Decreasing the particle size of the pigment increases its water-holding properties.

Other Colloidal Properties

The surface tension of the coating mixture is important when the coating is applied by roll coater, because this property has an effect on the size of the ribs which are formed by the action of the coating rolls. Surface tension is, of course, related to the wetting qualities of the coating mixture, and hence affects the penetration of the coating into the base paper. Many of the ingredients used in the coating formula, such as eveners and anti-foaming agents, have a pronounced effect on the surface tension.

The colloidal stability of the coating mixture is important, particularly when the coating mixture is held at the mill for several days before it is used. Colloidal instability is manifested by a change in viscosity of the coating mixture upon standing. If the coating mixture contains starch as the adhesive, there is likely to be an increase in viscosity caused by retrogradation of the starch. On the other hand, if the coating mixture contains casein as the adhesive, thinning generally results from the hydrolytic effect of the alkali on the casein. Willets[119] found that casein coating mixtures made with silicate as the dispersant markedly decreased in viscosity on standing, whereas mixtures made with sodium hexametaphosphate as the dispersant increased in viscosity on standing. In addition to these effects, spoilage may occur if the coating mixture is allowed to stand around for several days in hot weather. Spoilage reduces the viscosity of the adhesive, but the coating mixture itself may thicken, on account of flocculation of the clay by the acid produced during spoilage. Even a slight amount of spoilage will result in an appreciable decrease in the strength of the coating before there is any apparent odor. For these reasons, coating mixtures should be protected by preservatives if they are to be held for any length of time.

The presence of oil or grease in the coating mixture may result in oil spots due to poor wetting of the paper. Oil or grease may be present as a result of contamination from leaky bearings, too high a fat content in casein or animal glue, or too much soluble oil (e.g., pine oil) added as an anti-foam.

Foam

Foaming of the coating mixture is a frequent source of trouble to the coating mill chemist. Pinholes, visible with a hand lens or even with the naked eye, are produced as a result of foam breaking and forming a hole in the semi-dried coating. In some cases, foam may become so excessive as a result of air being whipped into the coating mixture that the coating mixture loses its fluidity and becomes difficult to handle.

Foam is of two types, coarse and fine. Coarse foam, commonly called froth, collects on top of the coating mixture and ordinarily is not troublesome. Fine foam remains dispersed throughout the body of the coating mixture. It is usually very troublesome and is difficult to remove, once it has been allowed to form.

Agitation, whether it takes place in mixers, pumps, or pipelines, greatly increases foam by whipping air into the coating mixture. Consequently, excessive agitation should be avoided as much as possible. Common causes of foam are open pipelines which discharge the coating mixture into open tanks, and leaky pumps which suck air into the coating mixture. In roll coating, air may be whipped into the coating mixture by the action of the rolls. Spoilage often causes a foamy condition, due to the liberation of gas bubbles from the decomposing adhesive. This type of foam is almost impossible to eliminate. If the coating mixture contains calcium carbonate, a drop in *p*H (due to spoilage or other causes) will cause excessive foam.

All lots of casein do not foam to the same extent; some caseins foam very little, whereas others foam very badly.[120] Mixing a foaming casein with a non-foaming casein usually results in a non-foaming mixture, indicating that lack of foaming is due to the presence of a natural anti-foaming agent in non-foaming casein. The use of sodium carbonate as a dispersing agent for casein causes foam, because of the carbon dioxide which is released when the carbonate is neutralized by the acid groups in the casein. Sutermeister[121] points out that if only slightly more than the theoretical amount of sodium carbonate is used, casein tends to foam badly, whereas if greater than the theoretical amount of sodium carbonate is used, the foaming tendency is reduced. He offers the explanation that the carbon dioxide is absorbed by the excess carbonate with the formation of bicarbonate. If casein dispersed with carbonate foams badly, the addition of ammonia or other alkali in addition to the carbonate reduces the foaming.

It is seldom that starch coating mixtures give any trouble with foam. Even oxidized starches, which are most likely to foam, rarely cause any trouble in coating mixtures. Dextrins which have been neutralized during manufacture with sodium carbonate are likely to foam badly; hence, other alkalies such as sodium phosphate or borax, which do not decompose to produce carbon dioxide, are used for neutralizing dextrins. Soybean protein has by nature a strong foaming tendency, even more so than casein, but commercial soybean protein contains an anti-foaming agent.

Most coating mills use some type of anti-foam to control foaming. This anti-foam is added as a regular part of the coating formula as insurance against the occurrence of foam, since foam has a tendency to appear and disappear for no apparent reason. Among the materials used as anti-foams are the sulfonated oils, pine oil, amyl or other high molecular weight alcohols, skim milk, ether, kerosene, tributyl phosphates, other petroleum fractions, and certain proprietary mixtures sold under trade names. These last are generally surface tension depressants which convert the fine foam into froth, which is then dissipated at the surface of the coating mixture. McGinn[122] recommends the use of metallic soaps. General experience has been that the addition of an anti-foam to a coating mixture which has already begun to foam does very little good. Best results are obtained by adding the agent either to the pigment dispersion or to the adhesive solution before the two are mixed together. Most chemists prefer adding the anti-foam to the pigment while it is being dispersed in water.

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[120] E. O. Whittier, S. P. Gould, R. W. Bell, M. B. Shaw and G. W. Bicking, *Ind. Eng. Chem.* 25, No. 8: 904–908 (Aug., 1933)

[121] E. Sutermeister, *Paper Mill News* 64, No. 25: 76, 78 (June 21, 1941)

[122] E. P. McGinn, *Paper Ind.* 27, No. 9: 1368–1371 (Dec., 1945)

Coating Raw Stock

Pigment coatings hide or cover up some imperfections in the base paper. This fact has caused some paper chemists to regard the base paper as of little importance, except as a mere carrier for the coating, and it has led, in some cases, to the use of inferior base stock. Actually, however, the properties of the body stock have a great influence on the quality of the finished coated paper. Milham[123] regards the base paper as presenting the most important technical problems for the paper coater. Among the properties of the base paper which are of importance are the formation, color, finish, sizing, strength, moisture content, porosity, brightness, and opacity.

Composition of Base Paper

Most coating raw stock is made from lightly beaten, weakly sized stock. Coating raw stock is classed as a special grade of book paper and is usually made and finished in the same general manner as book paper. A mixed furnish containing bleached sulfite and either soda or deinked stock has long been considered the ideal furnish. Several mills are now using sulfate pulp in place of sulfite particularly when high coat weights are to be applied. Some grades contain a proportion of rag pulp to improve the folding properties. Groundwood offers excellent possibilities, and it is likely that increasing amounts of groundwood pulp will be used, particularly bleached groundwood. Several typical examples of coating raw stock furnishes are given in Table XI.

TABLE XI

TYPICAL EXAMPLES OF COATING RAW STOCK FORMULAS

Furnish	Example No. 1, %	Example No. 2, %
Fiber		
Bleached sulfite	50	25
Soda	50	65
Sulfate	..	10
Non-fibrous, % of fiber		
Rosin size	0.50	1
Alum	1.0	1.5
Filler	5 (clay)	10

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[123] E. G. Milham, *Paper Mill 60,* No. 47: 15, 24, 26 (Nov. 20, 1937)

Bearse and Barclay[124] list the structure of a typical coating raw stock as follows: 50 to 25% supporting fibers, 40 to 70% filler fibers, 5 to 15% filler pigment, 1 to 10% sizing and other ingredients, 40 to 60% air. The supporting fibers (e.g., sulfite) supply the strength and flexibility, and consequently should be as continuous and as well bonded together as possible. The filler fibers (e.g., soda) furnish resiliency and bulk and act as the base for the coating. The filler (e.g., clay) contributes to the brightness and increases the receptivity of the paper for the coating. The air space makes the sheet receptive to the coating mixture and, in addition, supplies the printing cushion. The sizing in the sheet regulates the receptivity of the paper to the coating and the amount of penetration of the coating into the paper.

Sizing

In most grades of coating raw stock, light to medium sizing is used, but the optimum amount of sizing depends upon the properties of the coating mixture and the type of coating process. The subject of raw stock sizing is discussed in more detail in a later section.

Considerable interest has been shown in the use of wet-strength paper for coating rawstock.[125] A degree of wet strength is desirable because it helps to prevent breaks during the coating operation, thereby permitting the use of weaker pulps in the raw stock. Because wet-strength papers have better dimensional stability, less trouble with curl would be expected. Increased wet bonding of the surface fibers would prevent their being rubbed up and worked into the coating.

Finish and Porosity

Two highly important properties of the base paper are finish and porosity.[126,127] In general, coating raw stock should be well closed, i.e., not too porous, and the surface should be smooth, even, and free from imperfections. In machine coating, it is common practice to pass the paper just before coating between two heavy rolls known as smoothing rolls or breaker stack. These are usually steel or chrome-plated rolls operated at a pressure up to 100 lb. per lineal inch of nip and often are water-cooled to prevent sticking of the paper. Coating raw stock should not have too high a finish, since this results in a weak bond between the coating and the paper.

High bulk is desirable in coating raw stock because it permits more uniform calendering of the coated paper without producing hard spots. A soft, bulky sheet will coat better than a hard sheet because it has less tendency to curl. Furthermore, a soft bulky sheet is more resilient and forms a better cushion when the coated sheet is printed. The bulk must not be too high, however, since the strength of the paper will then be deficient.

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[124] N. I. Bearse and E. H. Barclay, *Paper Trade J. 120,* No. 12: 24, 26 (Mar. 22, 1945)

[125] R. W. Kumler, *Year Book,* Am. Pulp Paper Mill Supts. Assoc. 1945: 202–203

[126] F. H. Frost, private communication to the author (Jan. 17, 1947)

[127] N. I. Bearse and E. H. Barclay, *Paper Trade J. 120,* No. 12: 26 (Mar. 22, 1945)

Strength of Raw Stock

The strength of the raw stock is important because it is related to the strength of the final coated sheet. High tearing strength and high folding endurance of the body stock are good indications of the amount of handling the coated paper can stand. A high degree of fiber bonding is desirable, because this in part determines the resistance of the coated sheet to picking during the printing operation. In particular, the surface fibers of the base paper should be well bonded to the body of the sheet in order to prevent their being rubbed loose and worked into the wet coating. In general, it may be stated that increased beating of the base stock tends to increase the over-all strength of the coated sheet (see Table XII). By the same token, the presence in the raw stock of substances such as rosin and clay causes a reduction in the strength of the coated sheet. The base paper must not be too hard and dense, since this causes troubles such as curling and streaky coatings.

Brightness and Opacity

To the casual observer, it would appear that the color, cleanliness, and brightness of coating raw stock are of little importance, inasmuch as the paper is covered by a layer of coating. This would be true if thick coatings were applied, but in most commercial papers, the layer of coating is thin enough that the raw stock determines in part the brightness of the coated paper. For this reason, it is desirable to use bright, clean paper for coating raw stock. If light coatings are applied, the body stock should have a brightness as close as possible to that of the coating. Roll marks, brush marks, or other imperfections in the coating will be less conspicuous if the coating and raw stock have the same brightness than if the raw stock is appreciably darker than the coating. Large dirt specks should be avoided in the raw stock, since these tend to show through even the heaviest coatings.

Opacity of the raw stock is an important factor when light-weight coatings are applied. As a rule, groundwood papers make the most opaque raw stocks, and papers made from well-beaten rag or chemical wood pulps make the least opaque raw stocks. Fillers in the raw stock help to increase the over-all opacity, as does increasing the basis weight of the raw stock. The various factors affecting the brightness and opacity of coated papers are discussed later in more detail.

Uniformity

Uniformity in the coating raw stock is of the greatest importance. The weight, thickness, finish, smoothness, and the porosity should be as uniform as possible across the width of the sheet.[128] Paper which is wild tends to absorb coating unevenly, resulting in a mottled coating. Two-sidedness of the raw stock causes trouble if the paper is coated on both sides, inasmuch as the printing qualities of the coating will not be the same on both sides.

Applying Coating to Paper

One of the least understood phases of the coating process is the one involving the application of coating mixture to the base paper. This is, however, a very important phase, because it is during this period that the components of the coating mixture adjust themselves to their final state on the paper.

The film thickness of a wet coating is about 0.0014 to 0.0017 in. for a book paper coated with 25 lb. of coating per ream, 25 × 38—500 basis coated two sides, using a coating mixture between 35 to 40% dry solids.[129] After drying, the film of coating is approximately 0.0005 in. or 15 microns in thickness. On machine-coated papers, the wet film thickness is even less, being about 0.0005 in. (for an 8-lb. coating applied to one side, using a coating mixture of 60% solids). These thin layers require very fine machine adjustments in order to obtain an absolutely smooth and level coating.

Wetting of Raw Stock by Coating Mixture

The initial wetting of the raw stock by the coating mixture is important. Most coating mixtures readily wet the raw stock, on account of the natural affinity of the coating ingredients for the paper. In casein coatings, this wetting is augmented by high *p*H; Cobb and Lowe[130] point out that casein coating mixtures wet paper more rapidly than water. There is a tendency for wetting to be increased by the action of the brushes in brush coating and by the action of the rolls in roll coating. Once the coating has been properly applied, it must be maintained in place until it is thoroughly dried. The flow properties of the coating mixture must be such that the coating will not run and produce an uneven or wavy coating.

Measurement of Penetration of Coating Mixture into Raw Stock

The period during which penetration can take place is of short duration, since most coatings are substantially set within four to seven seconds after application. This short period of penetration makes penetration a difficult subject to study. Furthermore, the coating mixture may penetrate into the raw stock in one or more of three different ways: (*1*) the coating mixture may penetrate as a whole, (*2*) the adhesive may preferentially penetrate into the sheet, leaving the pigment behind, or (*3*) the water in the coating may penetrate to a greater extent than either the adhesive or the pigment. It has been stated that the casein in casein-clay coating mixtures penetrates the raw stock at least 3 microns beyond the farthest penetration of the pigment.[131] Segregation of the pigment and the adhesive may occur as a result of the gravitational pull during drying.[129] If this occurs, the pigment would tend to settle to the paper surface, leaving a thin layer rich in adhesive at the surface of the coating. On the bottom side of the sheet, the reverse would occur, namely, a layer rich in pigment would tend to form on the exposed surface of the coating. Obviously, these effects, if important at all, would be most pronounced in coatings containing pigments of high specific gravity. If mixed pigments were used, there might be a tendency for the heavier pigments to settle to a greater extent than pigments of lower specific gravity. This difficulty is common in the drying of paints, and sometimes leads to a change in the color of the paint, which is referred to by paint technologists as "flooding" or "floating."[132]

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[128] J. J. Friel, *Paper Mill News 64*, No. 49: 50–56 (Dec. 6, 1941)
[129] H. R. Rafton, *Paper Trade J. 94*, No. 3: 28–30 (Jan. 21, 1932)
[130] R. M. Cobb and D. V. Lowe, *Paper Trade J. 98*, No. 12: 43–46 (Mar. 22, 1934)

There is no very good method of measuring penetration. Singleterry[133] used a microscope to measure the depth of penetration by embedding a sample of the coated paper in a liquid mixture of urea-formaldehyde resin and zinc chloride, which was then allowed to harden, and finally was ground and polished into a section about 10 to 20 microns in thickness. Casey and Libby[134] used a microscope for measuring the depth of penetration of starch in starch-clay coatings by trimming one edge of the coated sheet, staining with iodine solution to bring out the starch, and then examining under the microscope, using reflected light. Phillips[135] measured adhesive and water retention by removing wet coating from the base paper by scraping at various time intervals and measuring the solids content and ash content of the wet coating layer. Lafontaine[136] and others suggest that an angle of contact test be used on coated papers to indicate the amount of adhesive which has left the coating.

[131] R. M. Cobb, *Paper Ind. 12,* No. 4: 753 (July, 1930); *J. Rheology:* 158–166 (1930)

[132] S. Hoagland, "The Rheology of Surface Coatings," R–B–H Dispersions, Inc. (1946)

[133] C. R. Singleterry, *Paper Trade J. 113,* No. 18: 233–236 (Oct. 30, 1941)

[134] J. P. Casey and C. E. Libby, *Paper Trade J. 127,* No. 25: 522–529; No. 26: 530–536 (Dec. 16, 23, 1948)

[135] J. Phillips, Thesis, "Study of Properties and Structure of Pigment Coatings," New York State College of Forestry, Syracuse, N. Y. (Dec., 1949)

[136] G. H. Lafontaine, *Paper Trade J. 113,* No. 6: 63–65 (Aug. 7, 1941)

Effect of Penetration on Properties of Coated Paper

Penetration of water and adhesive into the base paper affects the spreading properties, the strength of the coating, and the ink receptivity of the coating. There must be some penetration of coating into the paper in order to anchor or bind the coating to the paper, but the coating must not strike into the paper to an excessive degree. There is an optimum water and adhesive transfer from the wet coating to the paper for proper leveling of the coating, for best anchorage to the base stock, and for the prevention of dusting.[137] The penetrative qualities of the coating mixture must be adapted to the absorptiveness of the base paper.[138]

When the coating mixture first comes into contact with the raw stock, the water penetrates and brings about a swelling and disarrangement of the surface fibers. Too much penetration of water at this point results in a distortion and wrinkling of the paper. After the initial penetration of liquid, the network of fibers on the surface of the paper becomes swollen, thus tending to block off the pores of the paper and inhibit further penetration of the coating mixture. There must be sufficient penetration of adhesive into the paper to cause an intimate filling-in of the undercut regions about the surface fibers so that these fibers are well bonded together.[139] However, excessive penetration of adhesive leads to a "starved" coating with greatly reduced strength and a tendency toward dusting on the calenders. Singleterry[140] points out that a strong coating shows a gradation of adhesive into the paper for a distance of about 1 to 2 microns. The effect of penetration on the strength of coated paper depends somewhat upon the treatment of the paper for reducing penetration, e.g., reducing penetration by increased sizing tends to reduce the strength of the coating, whereas reducing penetration by increased beating of the base stock tends to increase the strength of the coated sheet. In the latter case, however, strength of the coating is more affected by changes in the strength of the base paper than by changes in the depth of penetration of adhesive.

Some of the factors which affect the penetration of coating into the raw stock are as follows:[141] structure of the raw stock, rheological properties of the coating color, surface chemistry of the fibers and the coating ingredients, conditions of coating, such as pressure and speed, and conditions of drying. These include machine conditions, properties of the coating mixture, and properties of the paper. All are important and are related to each other in complex fashion.

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[137] B. W. Rowland, *Paper Trade J. 112*, No. 26: 311–313 (June 26, 1941)
[138] G. K. Dickerman, *Paper Mill 61*, No. 53: 15–19 (Dec. 31, 1938)
[139] G. Davidson, *Paper Mill News 79*, No. 19: 14–16 (May 7, 1949)
[140] C. R. Singleterry, *Paper Trade J. 113*, No. 18: 233–236 (Oct. 30, 1941)
[141] N. I. Bearse, Private communication to the author (Jan. 7, 1947)

Effect of Properties of Coating Mixture on Penetration

The properties of the coating mixture which influence penetration are viscosity, yield point, degree of anomalous flow, water retention, per cent solids, and *p*H. It is well known that high-solids coating mixtures produce stronger coatings than low-solids coating mixtures for the same per cent composition. This effect has been ascribed to the reduced migration of adhesive from the coating layer, in the case of the coating of high solids content. Phillips[142] found, however, that increasing the solids content of the coating mixture decreased adhesive retention in the coating layer in spite of the fact that the strength of the coating was increased. The greater strength of the high solids coating, despite the lower adhesive retention, can be attributed to better distribution of adhesive in the base paper. The over-all viscosity of the coating mixture is made up of two components, the viscosity of the mineral component and the viscosity of the adhesive component. It is the viscosity of the adhesive component which is primarily responsible for the extent of penetration of adhesive into the paper. Thus, if the viscosity of the coating mixture is held constant while the solids content is increased, the penetration of adhesive into the paper will actually increase because of the lower viscosity of the adhesive which is present. Some coating mills make it a practice, when testing coating adhesives in the laboratory, to make tests at several different solids content in order to determine the effect of solids content on strength. As a general rule, coatings containing starch as the adhesive lose more in strength than coatings containing casein as the adhesive when the solids content of the coating mixture is reduced.

Increasing the *p*H of the coating mixture tends to increase the penetration of the coating mixture into the paper. The optimum *p*H depends upon the degree of sizing of the raw stock; hard-sized raw stocks work best with coating mixtures of higher *p*H value. The optimum *p*H value of the coating mixture is generally between 7.0 and 9.0, depending upon the degree of sizing in the base paper. Coating mixtures containing precipitated calcium carbonate may have a *p*H up to 10.0, due to the presence of free alkali in the carbonate.

Effect of Raw Stock Properties on Penetration

The important properties of the raw stock which determine the amount of penetration are sizing, porosity, and moisture content. The adhesive in the coating mixture will tend to penetrate into the paper beyond the pigment if the base paper is weakly sized. If a given coating mixture is applied to two raw stocks differing widely in sizing, the ink receptivity of the coating will be higher in the case of the weaker sized rawstock, indicating that more of the adhesive has penetrated into the paper.[143]

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[142] J. Phillips, Thesis, "Study of Properties and Structure of Pigment Coatings," New York State College of Forestry, Syracuse, N. Y. (Dec., 1949)

The optimum sizing for the raw stock depends upon the characteristics of the coating mixture. Casein coating mixtures require less sizing in the raw stock than starch coating mixtures.[144] High-viscosity coating mixtures require less sizing in the raw stock than low-viscosity coating mixtures. Dickerman[145] reports that unsized papers work best for machine coating, the absorbency of the paper being controlled by the type of furnish and degree of beating. Milham[146] points out that there appears to be an advantage in maintaining the body stock at a *p*H of 5.5 to 6.5 for starch-coated sheets.

The effect of rosin size on penetration is due primarily to a lowering of the contact angle between the liquid in the coating mixture and the paper. However, the electrostatic charge on the pores of the paper is also of importance. Rowland[147] points out that the starch adhesive in a starch-clay coating mixture will penetrate readily into the sheet if the paper is negatively charged, whereas if the paper is positively charged, penetration will be hindered. These effects are independent of water penetration effects, since they occur on unsized papers.

Another property influencing penetration of adhesive is the moisture content of the base paper. It was found in the early trials on machine-coated papers that coatings applied to wet paper (50 to 70% moisture) were lacking in strength. This was caused by excessive penetration of adhesive into the paper in the same way that a damp towel absorbs water faster than an absolutely dry towel. Hence, in the production of machine-coated papers, it was found advisable to control the moisture content of the base paper within limits, usually between 10 to 15%. If the paper has a much higher moisture content than this, the adhesive in the coating will soak into the paper excessively. On the other hand, if the base paper is too dry, the coating will not bond properly. The depth of penetration of starch in a starch-clay coating mixture increases linearly in unsized base paper as the moisture content of the sheet is increased from 0 to 48%.[148]

Pigment coatings do not dry evenly, but instead form dull and shiny spots during drying. This uneven drying is caused partly by uneven application of coating, with the result that the thinner spots dry faster than the thicker spots, and partly to a lack of uniformity in absorbency of the base paper caused by uneven calendering or sizing. Davidson[149] and Cagle[150] showed that the spots which are the last to become dull during the drying of the coating are the spots which show the least receptivity to ink, and are the most susceptible to picking. It is believed that the adhesive shows less penetration into the base paper in these areas, thus accounting for the low ink receptivity and poor strength.

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[143] J. P. Casey and C. E. Libby, *Paper Trade J. 127,* No. 25: 522–529; No. 26, 530–536 (Dec. 16, 23, 1948)

[144] N. I. Bearse and E. H. Barclay, *Paper Trade J. 120,* No. 12: 26 (Mar. 22, 1945)

[145] G. K. Dickerman, *Paper Mill 61,* No. 53: 15–19 (Dec. 31, 1938)

[146] E. G. Milham, *Tappi Bull. 57* (Aug. 6, 1945)

[147] B. W. Rowland, *Paper Trade J. 112,* No. 26: 311–313 (June 26, 1941)

[148] J. P. Casey and C. E. Libby, *Paper Trade J. 127,* No. 25: 522–529; No. 26: 530–536 (Dec. 16, 23, 1948)

Smoothing the Coating

After the coating has been applied to the paper, it must be smoothed or made level. When first applied to the raw stock, the wet coating is usually in a roughened condition, due to the brush or roll marks left on the surface. Immediately after application, the coating tends to spread out and produce a level surface on account of the force of surface tension. The important factor is the flow behavior of the coating mixture during and immediately after the coating has been applied to the paper and subjected to the agitation of the coating rolls or coating brushes. The leveling properties depend upon the water-holding capacity of the coating layer, because too rapid penetration of water into the base paper tends to set the coating before it is level. The requirements for proper leveling of the coating depend upon the type of coating process.

In brush coating, the coating mixture should be fluid under small shearing stress and have little or no yield point so that the brushes can spread the coating evenly over the surface of the paper. Part of the work of brushing is consumed in overcoming the viscous resistance to flow, and part is used in breaking down the structural resistance (thixotropy). The coating mixture must not have too high a viscosity, since this will prevent even spreading, but on the other hand, the coating mixture must not be too fluid, since this causes running. It should have a high water retention in order to retain its fluidity long enough after application to the paper to be smoothed out by the action of the smoothing brushes. The rate of body build-up after brushing should not be too rapid, inasmuch as this prevents after-flow and tends to leave brush marks in the coating. In order to meet the above requirements, it is customary to use coating mixtures of low solids content. Either casein or starch can be used as the adhesive in brush coating formulas.

In air knife coating, the coating is smoothed by the action of a fine air jet which blows across the surface of the coated paper. Ordinarily, this type of coater produces a very smooth coating, even on rough-surfaced papers. In general, the requirements of a coating mixture for air brush coating are similar to those for brush coating, although coating mixtures of somewhat higher solids content and somewhat higher viscosity can be used in air brush coating. Anything which disturbs the air stream, such as dried coating on the lip of the air slot, will cause streaks in the coating.

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[149] G. Davidson, *Paper Trade J. 110,* No. 24: 318–320 (June 13, 1940)

[150] J. H. Cagle, U. S. 2,286,259 (June 16, 1942)

The requirements for roll coating are quite different from the requirements for brush or air knife coating. Coatings appiled by roll coaters must set very rapidly, and hence high-solids coating mixtures are used. The viscosity is high, and in some cases, the coating mixture is semiplastic at the time of its application to the paper. When the print roll separates from the paper, the coating is "necked out" which leaves ribs or ridges in the wet coating film. The size of these ridges is determined by the forces of surface tension, flow properties, rate of shear at the nip of the rolls, and the rate of separation between the coated paper and the depositing roll.[151]

The coating is subjected to very high rates of shear in the nip of roll coaters, due to variation in peripheral velocity at different points in the nip caused by a difference in the softness of the rolls and by the fact that at some point in the nip the coating color is substantially stationary while the rolls are moving at high speed. The shear to which the coating is subjected in the roll nip causes radical changes in the flow behavior. In the case of thixotropic mixtures, this results in a thinning out and leveling of the coating on the paper. The effectiveness of thixotropy in eliminating surface pattern can be explained in a number of ways. The original theory was that thixotropy resulted in after-flow similar to that which occurs in freshly applied paint, but this effect is now believed to be of minor importance in paper coating because of the limited time involved before the coating is set. A more acceptable theory than the above is that the rate of shear in the roll nip (of the order of 10^4 and 10^6 reciprocal seconds) is at a maximum at the face of the roll, and since the viscosity of thixotropic mixtures is least where the rate of shear is greatest, the coating tends to rupture close to the roll surface. A contributing factor is the setting or solidification of the coating which occurs next to the paper surface, resulting from the absorption of water by the paper; this prevents any lateral displacement of the coating on the paper.

The degree of thixotropy required to obtain a pattern-free design in roll coating varies with the other flow characteristics of the coating mixture; for example, pseudoplastic mixtures require less thixotropy than Newtonian or plastic coating mixtures. The best available measure of the leveling properties is the so-called leveling index, the ratio of the coefficient of shear thixotropy to the plastic viscosity. The calculation of this index has already been discussed (see section "Flow Properties of Coating Mixtures"). Non-thixotropic coating mixtures produce a more pronounced surface pattern than thixotropic mixtures because there is no point of minimum viscosity next to the roll surface. Dilatant coating mixtures produce

[151] J. F. Halladay, *Modern Packaging 17,* No. 10: 111–143 (June, 1944)

the worst results of all, since they exhibit a point of maximum viscosity next to the roll surface. Hence, dilatant coating mixtures produce large ridges or piles of coating on the paper, because of the increase in viscosity at the roll surface which increases the resistance to separation of the roll and coated paper surface. Such surface irregularities indicate a lack of sufficient fluidity in the coating mixture during the period when the coating is subjected to the action of the coating rolls.

The weight of coating applied is a factor in determining the leveling properties, since even with rheologically acceptable coating mixtures, there is a limited range of coating weights within which pattern-free coatings can be obtained.[152] If the coat weight is too low, a striped pattern is usually obtained, while if the coat weight is too high, a stippled pattern is usually obtained. The better the over-all leveling properties of the coating mixture, the wider the range of coat weight which can be applied without pattern.

Drying

Conventional off-machine coated papers are dried by two different methods, festoon drying and the straight-pass system. In festoon drying, the coated paper is looped over a series of wooden sticks and carried through a drying tunnel. In the straight-pass system, the coated paper is carried through a drier tunnel without being looped over sticks; if the paper has been coated on two sides, the paper must be supported by air blown against the sheet in the direction of sheet travel until it is dry enough to come into contact with a festoon or some other type of carrier. The temperature of drying is quite important, and there has been considerable discussion among paper coaters about high-temperature versus low-temperature drying. Festoon drying represents low-temperature drying, i.e., about 120 to 150° F., whereas the straight-line system represents high-temperature drying, i.e., 250 to 300° F. Festoon drying generally takes from twelve to fourteen minutes, and this long drying cycle permits a uniform drying and allows the paper to assume its final shape without being subjected to tension or uneven temperature. High-temperature drying in the straight-line system is more likely to produce overdrying, curling, and warping than low-temperature drying, and may result in poor calendering conditions and a weaker coating. The sheet itself rarely reaches these high temperatures, however, because it is in a wet condition and therefore cannot exceed the wet bulb temperature at the humidity prevailing in the drier. In the coating of heavy insulating boards, it is customary to dry at temperatures in the neighborhood of 600 to 700° F.

Drying machine-coated papers is quite different from drying conventionally coated papers. Machine-coated papers are dried on the regular paper machine driers, using conduction for transferring heat. Very short air draws are used compared with the long air draws used in the drying of conventional coated papers. The drying of machine-coated papers must be carried out rapidly because of the short air draw. Care must be taken to have the driers immediately after the coater in good condition in order to prevent marking of the wet coating.

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[152] J. W. Smith, R. T. Trelfa and H. O. Ware, *Tappi 33*, No. 5: 212–218 (May, 1950)

The speed of drying depends upon the amount of water in the coating and the ease with which the water is released to the atmosphere. The ease of water removal depends on the degree of hydration of the various components in the coating. Coatings which contain hydrous clays are more difficult to dry than coatings containing non-hydrous clays. Coatings containing calcium carbonate are, as a rule, very easy to dry. Satin white tends to lose varying amounts of water, depending upon the temperature of drying.[153] It is customary to dry satin white coating at higher temperatures than those usually used on clay or clay-calcium carbonate coatings.

After the coating is dried, the paper is reeled and sent to the finishing department. The presence of coating on the underside of one-sided coated paper causes trouble in reeling and consequently should be avoided.

Calendering

Most coated paper is supercalendered. Supercalendering of coated paper is similar to the supercalendering of uncoated papers, except that cotton-filled rolls are used which are softer than the cotton- or paper-filled rolls used on uncoated paper. Machine-coated papers can be given a superficial finishing on the paper machine calenders, but in order to obtain a high finish, they must also be supercalendered. Machine-coated papers are generally supercalendered on a stack consisting of 10 to 12 rolls, at a pressure of 1000 to 2000 pounds per lineal inch, and at a speed of 1600 to 1800 f.p.m.[153a] Regular coated papers are generally supercalendered at lower pressures, e.g., 400 to 800 pounds per lineal inch.

The primary purpose of calendering is to increase the gloss and smoothness of the coating. In order to accomplish this, the coating must be plastic enough to smooth out under the pressure of the calender rolls without crushing the interior of the paper. If the coating is not sufficiently plastic, it will not produce a level surface, with the result that the gloss will be low. On the other hand, if the coating is too plastic, the paper will be blackened. Blackening is a phenomenon resulting in excessive loss of brightness, due to close compression and loss of light-refracting pigment surfaces. Albert[154] feels that blackening is caused by a shifting of the coating during calendering, resulting in the formation of ridges and valleys in the final coating.

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[153] J. D. Davies, *Paper Trade J. 113,* No. 2: 17–21 (July 10, 1941)

[153a] "Machinery for Coating," Tappi Monograph Series No. 8, p. 72, Tech. Assoc. Pulp & Paper Ind., N. Y., N. Y. (1950)

[154] C. G. Albert, *Paper Trade J. 105,* No. 6: 89–93 (Aug. 5, 1937)

The results obtained on calendering depend upon the type of pigment, type of adhesive, adhesive-to-pigment ratio, moisture content of coating, and presence of waxes or other ingredients. The most important single property in calendering is the moisture content of the coating. The higher the moisture content, the greater the smoothing, but the moisture in clay-coated papers at the time of calendering must not exceed 4 to 4.5% in order to avoid the danger of blackening. The critical moisture content is even lower for coatings containing satin white.

The pigment composition of the coating greatly affects the results obtained on calendering. Some pigments naturally take a much higher finish than others. Satin white, certain types of clay, and the fine photographic grades of blanc fixe produce very high finishes. Talc is another high finishing pigment and is used in friction or flint-glazed papers to the extent of 6 to 10% of the total solids. Calcium carbonate is usually classed as a dull finishing pigment, but certain grades can be made to produce a fairly high finish. The hydrous clays produce a higher finish on calendering than the less hydrous clays because of a greater shifting of crystal planes under the stress of calendering.[155] Calcined clay, which has no hydrating properties and presumably no crystal cleavage planes, produces coatings of relatively low gloss. Some pigments blacken more readily on calendering than others. Most clays will blacken if the moisture content of the coating is over 4% or if too much pressure is used, the hydrous clays being particularly bad. Calcium carbonate has less tendency toward blackening, and Roderick and Hughes[156] recommend the use of calcium carbonate with clay to reduce the blackening effect. With the dull finishing grades of calcium carbonate, the moisture content at the time of calendering can be as high as 7 to 8% without danger of blackening. The particle size of the pigment is an important factor affecting the calendering properties. In general, the finer the particle size, the higher the gloss after calendering. Fine clays show a greater loss of brightness on calendering than coarse clays,[157] but the initial brightness of fine clays is higher than that of coarse clays, so that the net effect is a coating of higher final brightness.

The amount of adhesive in the coating is another factor affecting the calendering operation. The higher the ratio of adhesive to pigment, the lower the finish of the coating after calendering. The type of adhesive is also important, since starch-coated papers do not, as a rule, calender to as high a gloss as casein-coated papers, but part of this difference is due to the higher percentage of adhesive generally used in starch-coated papers. The amount of adhesive in the coating is determined by the strength requirements, and ordinarily cannot be varied to regulate the finish.

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[155] B. W. Rowland, *Paper Trade J. 111*, No. 16: 207–212 (Oct. 17, 1940)

[156] A. E. Hughes and H. F. Roderick, *Paper Trade J. 109*, No. 11: 128–133 (Sept. 14, 1939)

[157] S. C. Lyons, *Paper Trade J. 106*, No. 26: 384–385 (June 30, 1938)

Calendering tends to lower the strength of the coating slightly, but the strength should not be lowered more than about a single wax (in the Dennison series) if the calendering operation has been properly carried out. A serious loss of strength as a result of calendering is indicative of lack of plasticity in the coating. If this occurs, the addition of plasticizers or an increase in the moisture content of the coating may be helpful.

Some coatings tend to dust on calendering, i.e., very fine particles of coating accumulate on the calender rolls. Coatings containing coarse pigments generally dust more than coatings containing fine pigments, since coarse pigments tend to spatter or break off the coating under the pressure of the calender rolls. Insufficient adhesive in the coating formula will cause dusting; dusting usually occurs on coated papers of low strength. However, dusting sometimes occurs on papers of high strength (as indicated by the wax pick test), in which case the dusting is probably due to excessive penetration of adhesive away from the top layer of the coating, leaving a thin surface layer which is deficient in adhesive and consequently tends to powder or dust. Dusting may also result from improper coating preparation, resulting in pigment agglomerates which have not been sized properly by the adhesive. Ordinarily, starch-coated papers dust more than casein-coated papers, but the latter are not entirely free from this trouble. Papers containing a high percentage of thermoplastic resin adhesive (resin emulsions) calender to smooth, high-gloss coatings without dusting. The dusting of starch-coated papers can sometimes be alleviated by the addition of suitable plasticizing agents, such as fatty acid soaps, wax emulsions, synthetic resin emulsions, and aqueous dispersions of insoluble metallic soaps. Dickerman and Riley[158] recommend the addition of 2 to 10% of ammonium stearate on the basis of the starch adhesive. The addition of a small amount of casein to a starch coating sometimes helps dusting. Dusting is one of those troubles which appear and disappear at intervals for no apparent reason.

Special Calendering Operations

There are several types of special finishing machines which are used on coated papers to produce special effects. One of the most important of these is the friction calender, which consists of a paper- or cotton-filled roll and one or two highly polished, chilled iron rolls which can be heated with steam or cooled with water. The coated paper is passed between the rolls with the coated side next to the iron roll. The iron roll is revolved at a peripheral speed which exceeds that of the filled roll by one and one-half to four times, and this produces a polishing action on the coating. An exceptionally high finish can be obtained on the friction glazing calender, but the process is limited because of high cost to a few special grades of coated papers, e.g., papers for box lining and other decorative purposes. Starch-coated papers are considered unsatisfactory for friction glazing because they tend to discolor from the heat generated in the process. Casein coatings containing a high finishing white pigment, some wax, and some talc are generally used. The amount of friction-glazed paper is limited because of the slow production speed, which is about 200 to 500 f.p.m. The nip pressure in friction calendering is generally about 300 pounds per lineal inch.

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[158] G. K. Dickerman and R. W. Riley, U. S. 2,425,231 (Aug. 5, 1947)

Another special finishing process is known as flint glazing. This is an ancient and almost obsolete process in which a flint stone is used for imparting an exceptionally high finish to the paper. In the early days, the paper was rubbed by hand, but in present-day machines, the paper is rubbed mechanically back and forth with a flint stone while the paper is held against a smooth wood surface or against wide leather straps. This process is used only where a very high finish and high bulk are desired, since it is extremely slow and expensive (speed about 7 f.p.m.). The greatest use is for fancy box coverings. A small amount of wax and talc are added to the coating formula to lubricate the coating and to impart an exceptionally high finish.

Another special treatment sometimes given to coated papers is that given in a brush machine. In this process, the coating is subjected to the action of rapidly revolving bristle or nylon brushes of graduated fineness while the paper passes over a large drum, after which the paper is supercalendered. The action of the brushes imparts a velvety or suede finish to the coating. The process is used mostly on high-grade coated papers containing satin white as part of the pigment.

Another method of obtaining an exceptionally high finish in coated papers is by cast coating. This type of coating involves the use of a large, highly polished nickel, Monel or chromium-plated drier against which the wet, freshly coated paper is pressed and allowed to adhere until thoroughly dry.[159] When dried in this way, the coating takes on the finish of the drier, making it possible to obtain a uniformly high finish as long as the surface of the drier remains unmarred. Care must be taken to see that there is no slippage of the coating against the drier and that no entrapped air is drawn into the nip. The moisture content of the paper at the time of stripping from the coating is rather critical. Wax is sometimes incorporated in the coating mixture to aid in stripping. The gloss obtained in the final paper increases with an increase in the amount of adhesive in the coating formula, which is different from the result obtained in regular calendered papers. The surface of the finished paper is soft and porous compared with ordinary supercalendered papers, and the coating tends to mar easily. Cast coating may be used as a machine coating process, or it may be used to apply a second coating on an already coated paper.

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[159] D. Bradner, U. S. 1,719,166 (July 2, 1929)

Coated papers receive special care in sorting because they must be relatively free of imperfections. Some of the common defects which occur in coated papers are brush marks from the coating brushes, roll marks, pinholes, oil spots, dirt specks, and cracked coating. In order to remove the imperfect sheets from the good ones, highly trained inspectors are used to sort the paper.

Evaluation of Coated Papers

Coated papers are of a large number of different grades, and new grades are constantly being developed. A few of the more important classical grades are listed below.

(*1*) *Coated book.* This is a general grade which includes all coated papers (e.g., magazine, pamphlet, book, and brochure) intended for printing or publication where fine halftones are used. The paper may be coated on one or two sides. The basis weight ranges from 40 to 150 lb. (25 × 38—500), 60 to 80 lb. being most common. The finish ranges from a dull mat to a high gloss. Coated art papers are used where exceptional finish is desired for special effects in halftone printing.

(*2*) *Coated label.* This is a paper used for printed labels which are coated on one side and often gummed on the other side. A similar grade is coated box cover or box enamel paper, which is light-weight paper coated on one side (but not gummed) for use in covering boxes.

(*3*) *Coated litho.* This is a coated paper used for printing by the lithographic process. It is usually coated on one side. The coating is specially sized to resist water on the lithographic blanket. A similar grade is coated offset paper which is usually coated on two sides.

Machine-coated papers, which have already been discussed, ordinarily contain less coating than regular book grades. They are used for magazines and for opaque bread wrappers. Coated wallpaper will be discussed later. Many grades of board are also coated, including board for folding boxes, coated blanks (for calenders and advertising) and wallboards.

Coated papers should be regarded as a special type of paper in which surface qualities far outweigh the other properties in importance. Coated papers often have low over-all strength and poor folding properties because these properties are of secondary importance. Coated papers are useful because the coating provides a smooth, even, and continuous surface which makes a far better printing surface than that provided by uncoated paper. The pigment in the coating is primarily responsible for these desirable properties; the purpose of the adhesive is to bind the pigment particles to one another and to the surface of the sheet so that the coating will not be pulled loose by the printing ink. Some of the important properties of coated papers are strength of the coating, smoothness, ink receptivity, brightness, and gloss.

Pigment-coated papers are a special grade of printing paper, and consequently they are evaluated by many of the same procedures used for uncoated printing papers. These procedures are described in Chapter XIX to which the reader is referred. The most satisfactory method of evaluating coated papers is by printing press runs, preferably on a commercial press, but if that is impossible, on a laboratory proof press. In testing on a press, selected samples of coated paper are run on the press under standardized conditions, and the resultant printing is graded for quality as excellent, good, fair, or poor.

Making Laboratory Coatings

Coating formulas can be readily tested in the laboratory by (*1*) making a small batch of coating mixture, using the proper adhesive and pigment combination, and (*2*) applying this coating mixture to a suitable sample of raw stock, using suitable small-scale equipment. One method of coating handsheets is by the brush-out method in which a special badger hair brush is used for spreading the coating over the surface of the paper. More satisfactory results can be obtained with film applicators, such as the Martinson coater or Bird applicator. The Bird applicator[160] is available in three sizes (0.0005, 0.0015, and 0.003 in.) for applying coatings of different weights. The Martinson coater[161] can be adjusted to apply coatings in any weight by raising or lowering the knife blade. With knife coaters, there is a tendency to apply heavier coatings as the viscosity of the coating mixture is increased and as the speed of the paper relative to the coating blade is increased. Another laboratory coating device in wide use consists of a metal rod spirally wound with wire. The amount of coating applied is determined by the size of the wire wrapped around the rod. This coating device is available in a large number of different sizes, so that a wide range of coating weights can be applied.[162]

A laboratory size air knife coater is available. This piece of equipment will coat sheets 8 × 23½ in. in size, and with special equipment, will handle a continuous web of paper. This coater (Microjet) is furnished complete with motor-driven coating roll drive and automatic air supply for the nozzle.[163] There is a special knife-type laboratory coater (Diatron coater) which is suitable for coating a continuous web of paper. A pneumatic diaphragm is used for holding the sheet against the knife blade.[163] This coater is equipped with radiant type heaters for drying the coated paper.

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[160] Bird Machine Company, East Walpole, Massachusetts

[161] Martinson Machine Co., Kalamazoo, Michigan

[162] R. D. Specialities, Rochester, New York

[163] John Waldron Corporation, New Brunswick, New Jersey

In addition to the above laboratory coating devices, there are many custom-built roll coaters which are used for coating paper in the laboratory. These roll coaters are constructed at the coating plant as small-scale replicas of the commercial coating machine used in the plant. These coaters make it possible to reproduce conditions in the laboratory similar to those which are encountered in commercial operation.

Strength of Coating

The term "strength" has a different meaning when applied to coated papers than when applied to uncoated papers. In the case of coated papers, the strength refers to the resistance of the coating to the shearing stress of a viscous film such as occurs during the printing of the paper with a tacky ink. Ordinary tensile strength tests have very little significance for coated papers.

One of the earliest tests used to determine the strength of coated papers was the wet thumb test. In this test, the thumb was moistened, pressed firmly against the coating, and held there for a few seconds. The thumb was then removed and examined for bits of coating. This test was materially affected by the water sensitivity of the coating and proved unreliable in comparing starch- and casein-coated papers. However, in the hands of an experienced man, it served as a rough guide for comparing various casein-coated papers.

The next test to be employed was the sealing wax test. In this test, a piece of sealing wax was melted over a low-temperature gas flame and then was pressed against the coating and allowed to cool. After the wax was cooled, it was pulled from the coating and examined. Because the strength of the wax was high, some of the coated paper was always removed; the results were judged by whether the rupture occurred in the coating layer or in the base paper, or, in other words, whether the wax caused a coating pick or a body stock pick. The shortcoming of this test was that the strength of the coating was judged in relation to the strength of the base paper. Hence, with a weak base paper, the coating would appear strong by comparison, whereas with a strong base paper, the coating would appear weak by comparison.

In order to overcome the shortcomings of the above methods of testing, a new test was developed using a series of waxes of graded strengths. The commercial waxes[164] used for this purpose are made by mixing two or more waxes (e.g., bayberry and carnauba) in different proportions to obtain a series of waxes of graded strength or pull. The test is carried out by first melting the wax, then placing it against the coating, allowing it to cool for fifteen minutes, and finally removing with a gentle upward pull. The waxes are numbered from 2 to 12 or higher according to their strength. The results are reported as the highest wax which shows no pick. It is informative to report whether the pick is a coating or a body stock pick. This test is commonly called the wax pick test.

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[164] Dennison Wax Series, Dennison Manufacturing Co., Framingham, Massachusetts

Another method of using the wax test is to press a No. 12 Dennison wax on the paper in a special clamp having an opening exactly 0.5 in. in diameter, attaching the lower end of the clamp to the bottom jaw of a tensile tester and the end of the wax to the upper jaw, and then measuring the pull required to rupture the paper surface.

Inasmuch as waxes are widely used for the testing of coated papers, it is worth while to consider some of the factors which influence the wax test. Kirkpatrick[165] has listed the following factors as being most important, probably because they influence the crystal structure which is set up in the cooling wax at the surface of the coating: (*1*) rate of cooling of wax, (*2*) ultimate temperature of wax, and (*3*) humidity. High humidities and high temperatures cause the coating to pick at a lower wax number. Consequently, the wax test should be carried out under controlled conditions of temperature and humidity in order to obtain consistent results. Another important factor affecting the result is the moisture content of the coating, since some coatings are affected by moisture more than others. For example, the wax test on casein-coated sheets is only slightly reduced if the coating is wet, whereas that on starch-coated sheets is greatly reduced. Annis[166] has observed that a thin coating of casein applied over a casein-clay coating increases the wax test. This film of casein reduces the adhesion between the wax and the coating and does not actually strengthen the coating. Such a condition might occur during normal coating if the pigment should settle against the base paper, thereby leaving a layer rich in adhesive on the surface. The wax test is a measure of the adhesion between the wax and the surface of the coating, as well as a measure of the strength of the coating and base paper. This fact accounts for many of the apparent anomalies in results obtained with the wax pick test. A high wax test does not insure freedom from picking during printing, since a hard-sized paper may pass a high wax test because of lack of adhesion between the wax and the coating. However, when such a sheet is printed, tacky inks will be required to bond to the hard-sized surface, and these may be sufficiently strong to pull the body stock apart.

The proper interpretation of the wax test requires considerable experience and a knowledge of the use to which the paper is to be put. For example, Upright and coworkers[167] report that a higher wax number (about 1 wax higher) is required for casein-coated papers than for methylcellulose-coated papers in order to obtain a sheet which will not pick on the press under the same conditions of printing. Likewise, starch-coated papers sometimes require a higher wax number than casein-coated papers. Coatings containing satin white are usually stronger than the wax test would indicate. The type of printing process used for printing the paper must be taken into account. In general, the following wax tests are the minimum values required for the different grades of printing papers based upon the wax which shows no pick.[168] Higher pick resistance is required for certain types of printing (see Table III, Ch. XIX).

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[165] W. A. Kirkpatrick II, *Paper Trade J. 109,* No. 12: 156–158 (Sept. 21, 1939)
[166] H. M. Annis, *Paper Trade J. 96,* No. 2: 20–22 (Jan. 12, 1933)

Paper	Dennison wax	K & N wax
Uncoated offset	11	90
Coated letterpress book	4	15
Coated offset or litho book	6	60

According to Griswold,[169] coated paper for offset printing should pass a No. 8 wax, but normally a No. 6 wax is considered satisfactory. Papers for spirit varnishing will stand a higher wax, No. 9 or above. If the coated paper contains thermoplastic materials such as zein or rubber latex, the wax test is of limited value for judging the strength. One case has been reported[170] where a sheet with a wax test under 2 (which would normally be considered unprintable) was used in normal printing without trouble.

Because of its shortcomings, the wax test has been subjected to considerable criticism. Much of this criticism is justified, but it has been difficult to devise a satisfactory and, at the same time, simple means of evaluating the strength of coated papers. The best method of testing coated paper is by means of an actual printing press run on a commercial press, but as this is often not feasible, attempts have been made to duplicate the conditions existing on a printing press by means of less elaborate equipment. Most of these tests involve comparison with samples of paper of known printing qualities. Proof press runs using inks of varying tack are sometimes used to measure strength. In another simple test,[171] a flat tin plate having an opening 3 × 4½ in. is placed over a sample of standard paper of known printing properties and a sample of the unknown specimen so that one-half the area of the opening in the plate is covered by each sample. A brass roll covered with tacky ink is then rolled back and forth over the opening until one of the papers is picked. This gives a comparison of strength between the unknown and the standard sheet.

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[167] R. M. Upright, M. Kin and F. C. Peterson, *Paper Trade J. 114*, No. 2: 16–20 (Jan. 8, 1942)

[168] W. A. Kirkpatrick II, *Paper Trade J. 109*, No. 12: 156–158 (Sept. 21, 1939)

[169] W. E. Griswold, *Paper Ind. 29*, No. 2: 262–267 (May, 1947)

[170] O. P. Berberich, L. F. Engelhart and M. Zucher, *Paper Trade J. 127*, No. 7: 348–352 (Aug. 12, 1948)

[171] A. J. George, *Paper Trade J. 84*, No. 13: 39–40 (Mar. 31, 1927)

Several new types of pick testers operating on the principle of small variable speed printing presses have been introduced. These differ in construction, but are all designed to measure the critical speed at which picking occurs when a film of ink of predetermined thickness is applied to the paper under controlled conditions. The film of ink exerts a pull on the coating which increases as the speed is increased. The speed is varied during testing until the coating is ruptured, and the lowest speed at which rupture occurs is taken as the critical speed. In early instruments of this type, the ink was applied to a pair of finely polished rolls which were then rolled over the surface of the paper,[172] but in more modern instruments, the ink is applied to flat ink plates and the paper is clamped to the cyilnder. In one instrument of this type, known as the Warren M. P. tester,[173] a test strip (1½ in. wide) of standard coated paper of known strength and a strip of the unknown paper under test are clamped side by side on the surface of a rotatable cylinder. A plate bearing a printing ink film of controlled thickness is then driven at a known controlled speed into simultaneous printing contact with both strips. The speed of the printing block is increased until picking occurs on one paper, and then is further increased until it occurs on the other paper. Thus, a ratio of the relative strengths of the two papers is obtained. In another instrument, known as the Davidson-Pomper tester,[174] four samples of paper (½×6 in.) are placed on a rubber-covered gripper cylinder while a tacky testing ink (I.P.I. Tack Graded Black #6 – #8) is applied to two stainless steel ink plates. The instrument is then set at a speed near the value at which picking is expected to occur, and the inked plates are fed to the tester. The samples are then inspected for picking, and new tests are made on fresh samples at lower or higher speeds until picking occurs. The range of speed is 0 to 740 f.p.m. The ink temperature is controlled by means of a thermostatically controlled heater. Using an apparatus similar to that described above, Davidson[175] found that the relative critical speeds varied from 200 to 250 r.p.m. for coated letterpress papers to 250 to 500 r.p.m. for coated offset papers. The temperature of the test ink must be held within narrow limits, since temperature variations of 5° F. cause lack of reproducibility.

Some of the factors which affect coating strength are pigment composition, amount of adhesive used, type of adhesive used, method of preparation of coating mixture, solids content of coating mixture, properties of body stock, type of coating equipment, conditions of drying the coated paper, and type and degree of calendering. Strength of coated paper is a complex function of the strength of the coating layer, the strength of the base paper, and the type of bond formed between the coating layer and the base paper. From a strength standpoint, the coated sheet must be regarded as a whole. It is impractical to draw a sharp line of distinction between the coating and the base stock, inasmuch as the coating penetrates into the fibrous system, producing a gradual transition from coating to fiber. Singleterry[176] and Lee[177] have published photomicrographs showing the irregular boundary between the coating and the base paper. In some regions, individual fibers may become completely embedded in the coating, and in other regions, the coating may penetrate and fill voids deep in the body of the paper. During coating, the action of the brushes or coating rolls tends to disturb the surface fibers of the paper which results in better contact between the coating and paper.

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[172] Staff of the Institute of Paper Chemistry, *Paper Trade J. 123,* No. 18: 24–29 (Oct. 31, 1946)

[173] Made by S. D. Warren Co., Cumberland Mills, Maine

[174] Made by John Waldron Corp., New Brunswick, New Jersey

[175] G. Davidson, *Paper Mill News 72,* No. 19: 16–18 (May 7, 1949)

When the coated paper is ruptured, the zone of failure may occur in the coating itself, at the interface between the coating and the base paper, or in the body stock. Singleterry[176] found on coatings which are weaker than the body stock that the zone of failure occurs in the coating layer about 1 micron away from the interface, and in no case does failure occur at the interface. If the coating layer is mechanically stronger than the paper, the rupture will occur either at the interface or in the paper. The latter is known as a body stock pick, or if the picking occurs in large solid areas, it is known as splitting. Failure often occurs in the body stock at a lower wax number than that which causes picking on the uncoated raw stock.[178] The reason for this is that the wax bonds with greater tenacity to the coating than to the body stock so that there is actually a greater pull applied to the body stock when the coated paper is tested.

The most important factor determining the strength of coated paper is the amount of adhesive used in the coating formula. Increasing the amount of adhesive in the coating formula increases the bond between the pigment particles and also strengthens the surface of the base paper. If the coating has good strength, the practical coating man refers to the coating as "hard-sized" or, if weak, he refers to it as "soft-sized." A comparison of the pigment bonding strength of different adhesives has been shown in Figure XVIII-2. Increasing the amount of adhesive in the coating increases the wax pick test, even though the line of failure originally occurred in the base paper. Since it is doubtful if the adhesive penetrates sufficiently far into the base paper to increase the over-all strength of the paper, the increased wax pick test must be attributed to reduced bonding between the wax and the surface of the coating caused by the higher percentage of adhesive in the coating layer.

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[176] C. R. Singleterry, *Paper Trade J. 113,* No. 18: 233–236 (Oct. 30, 1941)

[177] H. N. Lee, *Paper Trade J. 107,* No. 6: 53–59 (Aug. 11, 1938)

[178] H. M. Annis, *Paper Trade J. 96,* No. 2: 20–22 (Jan. 12, 1933)

The properties of the pigment which affect coating strength have been discussed earlier in this chapter under adhesive demand of coating pigments (see Table VIII and Fig. XVIII-16). The important properties are type of pigment, particle size, and particle size distribution.

The strength of coated paper depends upon such properties of the raw stock as the amount of sizing agent, amount of filler, and the density of the paper. The effect of raw stock hardness on the strength of coated paper is shown in Table XII.[179]

TABLE XII

EFFECT OF RAW STOCK HARDNESS ON STRENGTH OF COATED PAPER AS MEASURED BY WAX PICK TEST

Raw stock	Wax pick test on raw stock	Wax pick test on coated sheet
Soft	6.5	4.2
Moderately hard	11.0	5.1
Very hard	16.5	6.6

Ordinarily there is a difference in the strength of the coating on the two sides of coated paper. As a rule, the coatings applied to the felt side are weaker than the coatings applied to the wire side,[180] although Singleterry[181] obtained better bonding on the felt side. These effects are related to the two-sidedness of the paper, i.e., to differences in sizing, filler content, and percentage of fines on the wire and felt sides of the raw stock. Other factors which influence the strength of coated paper have been discussed throughout this chapter.

Coating Weight

The weight of coating applied in commercially coated papers varies from 1 lb. per ream per side for the very lightest semicoated papers made on the paper machine to about 15 to 17 lb. per ream per side for the regular grades of brush-coated papers. According to present practice, a 60-lb. litho coated one side generally contains about 15 to 16 lb. of coating per ream; a 70-lb. letterpress sheet coated both sides generally contains about 12 to 13 lb. of coating per side; and a 55-lb. machine-coated magazine paper coated both sides generally contains about 8 lb. of coating per side. Highly filled book papers, e.g., regular supercalendered book paper, may be given a very light coating on only the wire side in order to replace the filler lost through the wire.

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[179] C. G. Landes, *Paper Trade J. 110,* No. 11: 152–160 (Mar. 14, 1940)
[180] H. M. Annis, *Paper Trade J. 96,* No. 2: 32–34 (Jan. 12, 1933)
[181] C. R. Singleterry, *Paper Trade J. 113,* No. 18: 223–236 (Oct. 30, 1941)

Barytes-coated photographic papers may have up to 33 lb. per side, coating being applied in three successive coats. There is a trend in modern coating to apply two or more coats on the highest grades of letterpress and litho-coated papers. Both of these coats may be applied on the paper machine, or one coat may be applied on the machine and another off the machine or both off the machine. The clay contents of several typical coated papers are given in Table XXXVI in Chapter XVI.[182] The thickness of the dried coating film ordinarily varies from about 5 microns on machine-coated papers to about 12 to 15 microns on brush-coated papers.

It is sometimes desirable in analyzing coated papers to determine the amount of coating on the paper. This can be done, in the case of casein-coated papers, by (*1*) soaking the coated paper in a solution of suitable proteolytic enzyme to dissolve the adhesive and release the pigment and (*2*) gently brushing the wet coating with a soft camel's-hair brush until all visible coating is removed.[183] The amount of coating can then be determined by the difference in weight of the dried paper before and after the removal of the coating. Starch-coated papers can ordinarily be desized without using an enzyme. Coated papers containing a high percentage of synthetic resin emulsion cannot be desized readily, and consequently they pose a problem when it is necessary to determine the amount of coating on the paper. The desizing test can be used for determining the amount of adhesive in the coating, as well as the total weight of coating; this is done by taking the difference between the weight of the coating as determined above and the amount of mineral matter in the coating. The amount of mineral matter in the coating is obtained by subtracting the ash of the decoated paper from the total ash of the original coated paper after converting from ash content to corresponding mineral content.

The amount of coating applied to the base paper, i.e., the coat weight, affects the strength, ink receptivity, brightness, and opacity of the coated paper. The effects of coat weight on the strength and optical properties of coated paper are shown in Figure XVIII-22 taken from work by Landes.[184] These results were obtained using a casein-clay coating containing 13% casein on the weight of the clay applied to a moderately hard raw stock. Under these conditions, a coat weight of 15 to 20 lb. (25 × 38—500) was found to be the optimum point above which there were no further changes in the gloss and strength properties. However, the opacity of the paper continued to increase with further increases in coat weight. The effect of coat weight on brightness and opacity is discussed further in a later section. According to Landes,[184] increasing the weight of applied coating lowers the

[182] "Kaolin Clays and Their Industrial Uses," p. 127, J. M. Huber Corp., New York, N. Y. (1949)

[183] See TAPPI Standards

[184] C. G. Landes, *Paper Trade J. 110,* No. 11: 152–160 (Mar. 14, 1940)

ink receptivity and the wax pick test. In many cases, however, the ink receptivity is increased by increasing coat weight.

Water Resistance

Water resistance is an important property for those grades of coated paper which are likely to come into contact with moisture during use. Among these papers are washable wallpapers, coated tag, coated labels, coated decorative papers (e.g., Christmas wrappings), and coated paperboard for pharmaceuticals and soap boxes. Coated offset paper should have some water resistance, since the paper is subjected to conditions of high moisture during printing. It is desirable, although not necessary, to have a small degree of wet-rub resistance on all grades of coated book and magazine papers in order to prevent smudging during handling.

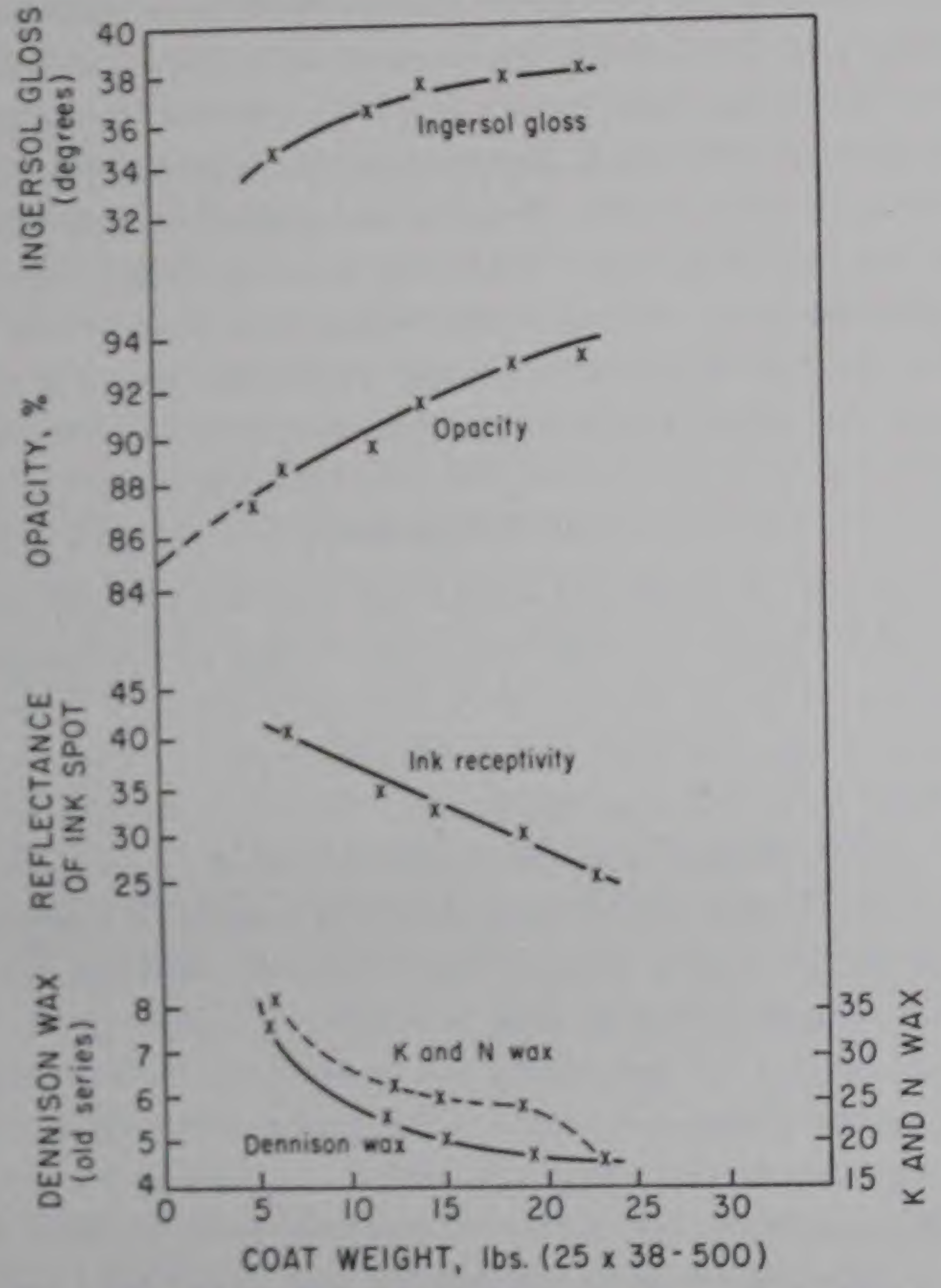

Fig. XVIII-22. Effect of coat weight on physical and optical properties of coated paper.

When coatings of high water resistance are required, casein or soybean protein is generally used as the coating adhesive. Either of these adhesives will produce a highly water-resistant coating, particularly if the coating has been hardened with formaldehyde. On the other hand, starch-coated papers are very sensitive to water, although it is possible to impart some water resistance to starch-coated sheets by the use of urea-formaldehyde resins as described earlier. Coated papers can be tested for water resistance by a simple method devised by Hewett and coworkers.[183] In this test, the coated paper is placed on a sheet of black paper so that 2 or 3 in. of black paper extend beyond the edge of the coated sheet. Next, a drop of water is placed on the coating and left for fifteen seconds to soften the coating. Then, while the two sheets are held firmly in place, the forefinger is drawn from the coated paper onto the black paper, using three successive strokes. This rubbing action transfers some of the coating to the black paper, leaving a white spot on the black paper when the coating dries. The intensity of this white spot varies according to the water resistance of the coating. A mechanical method of determining water resistance using a special device which brushes the paper while submerged in water has been described by Black.[184]

Ink Receptivity

Ink receptivity and ink absorption are two very important properties of coated papers. Improved ink receptivity is one of the important advantages which coated papers enjoy over uncoated papers. There is an optimum ink receptivity for each grade of coated paper, depending upon the type of printing to be done on the paper. For best results, the ink receptivity should be maintained near this optimum value. Too high a resistance to the penetration of printing ink is undesirable because it results in filling-in of the halftone screen and in slow drying of the ink on the paper. Too high ink absorption is undesirable because it results in a gray print.

The best method of measuring ink receptivity is to make an actual printing test on the paper and compare the quality of printing with a standard sample, but this is not always feasible. A simpler method of testing which is widely used involves the use of test inks such as the K & N testing ink, a special ink containing an oil-soluble dye dissolved in a non-drying varnish.* In this method of testing, the ink is applied to the surface of the coated paper by means of a roller or spatula under carefully controlled conditions. The essential requirements are: (*1*) to apply a heavy film of ink, (*2*) to allow the film to penetrate for a definite length of time (usually 2-4 minutes), and (*3*) to remove the excess ink and dry with a clean cloth. A numerical value for the ink receptivity is then obtained by measuring the reflectance of the inked sheet on a photometer. This gives an indication of the amount of ink which has been absorbed by the coating. The darker the inked spot, i.e., the more ink that is absorbed, the lower the reflectance. The brightness of the stained spot varies linearly with the logarithm of the elapsed time.[187] Usually a reciprocal of the reflectance reading is taken so that an increase in absorption of ink results in an increase in the numerical value for ink receptivity. This method of testing gives fairly good comparisons between coated papers containing the same pigment formulation, but different pigments in the coating produce different hues and prevent an exact quantitative indication of comparative ink receptivity.[188] If the coating is highly alkaline, the dye in the ink will be turned a purple color.

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[183] P. S. Hewett, R. E. Carter and R. J. Church, *Paper Trade J.* *124*, No. 24: 263-268 (June 12, 1947)

[184] W. C. Black, *Tappi* *32*, No. 10: 467-468 (Oct., 1949)

* Manufactured by K & N Laboratories, Inc., 410 N. Michigan Ave., Chicago, Illinois.

Other methods of measuring ink receptivity and oil absorption are described in Chapter XIX. Kirkpatrick[189] mentions the use of the wax test as a guide to the ink absorption of coated papers and suggests as a safe rule that the paper should show a Dennison wax test no more than 2 higher than that established as a minimum for strength.

A number of factors affect the ink receptivity and ink absorption of coated papers. The amount of adhesive in the coating is the most important factor. The lower the adhesive-to-pigment ratio in the coating, the higher the ink receptivity and ink absorption of the coating. Excessive penetration of adhesive into the base paper during coating increases the ink receptivity, since this reduces the amount of adhesive in the coating layer. Starch-coated papers have a higher ink receptivity than casein-coated papers when equal amounts of adhesive are used because of the weaker film-forming property of the starch. However, in coatings of equal strength, where more starch than casein is normally used, the ink receptivities are more nearly equal, and sometimes starch-coated papers have lower ink receptivity than casein-coated papers.

The type of pigment used in the coating is another important factor determining ink receptivity. The particle size of the pigment is important, inasmuch as pigments of large particle size produce coatings of higher ink receptivity than pigments of small particle size. The type of pigment is also important. Clays from different sources vary considerably in ink receptivity. Calcium carbonate pigments produce highly ink-receptive coatings, particularly the precipitated grades. As evidence of the strong ink receptivity of precipitated calcium carbonate, Roderick and Hughes[190] showed that coatings containing precipitated calcium carbonate have a higher ink receptivity than coatings made with clay, even when both are sized to the same wax pick test (where the calcium carbonate coating contains considerably more adhesive than the clay coating). The use of satin white in the coating formulation generally increases the ink receptivity of the coating, probably because of the porous nature of satin white coatings. The relationship between the strength and ink receptivity of coatings containing different pigments is shown in Figure XVIII-23.[191] Calendering also has an appreciable effect on the ink receptivity of coated papers, just as it has on uncoated papers.

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[187] A. Voet and J. S. Brand, paper presented at 35th Annual Meeting of TAPPI, New York City (Feb. 20–23, 1950)

[188] C. G. Landes, *Paper Trade J. 110,* No. 11: 152–160 (Mar. 14, 1940)

[189] W. A. Kirkpatrick, *Paper Trade J. 109,* No. 12: 156–158 (Sept. 21, 1939)

[190] A. E. Hughes and H. F. Roderick, *Paper Trade J. 109,* No. 11: 128–133 (Sept. 14, 1939)

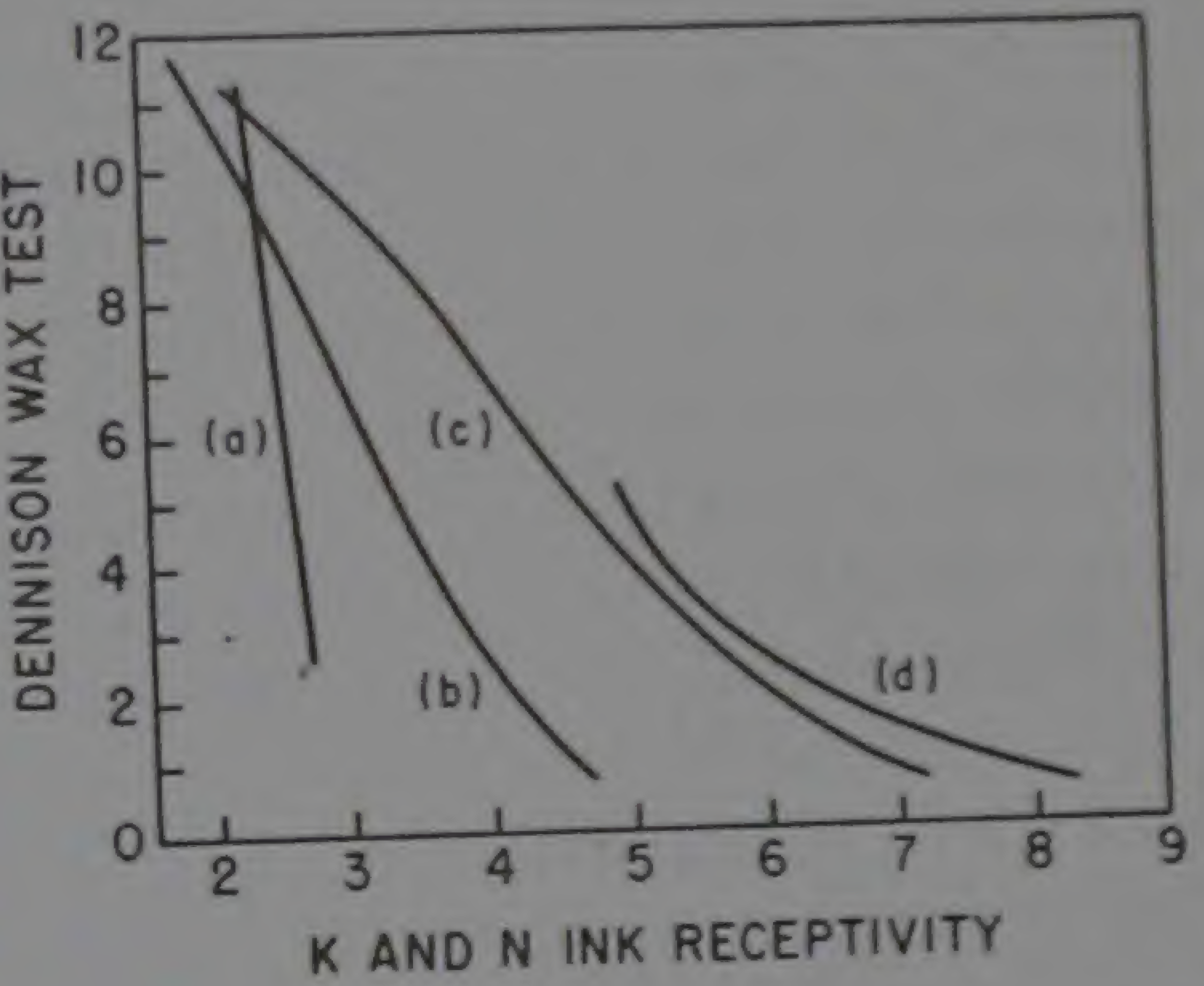

Fig. XVIII-23. Relationship between strength (wax number) and ink receptivity in coated papers[191] (a) titanium dioxide, (b) domestic clay, (c) calcium carbonate, (d) satin white.

Smoothness

One of the principal objects of coating is to obtain a smooth surface which will insure better contact between the paper and the printing plate than is possible with uncoated papers. The smoothness is determined by the contour or degree of continuity of the coated surface. Smoothness is usually measured by the rate of flow of air between two or more sheets of the coated paper, or between one sheet of the coated paper and a smooth standard surface, using the some procedure as for uncoated paper.

A rough-coated surface causes trouble in halftone printing by breaking the contour of the halftone dot, particularly in the light and middle tones. The size of a halftone dot for a 133-line halftone plate is about 0.074 mm. in diameter.[192] It is evident that dots of this small size will be distorted by even slight imperfections in the surface of coated papers. A good indication of the magnitude of the surface irregularities which will affect fine printing can be obtained by examining the coating with a hand lens or microscope magnifying between 20 to 50 diameters. Anything which shows up as being of appreciable size at this magnification will affect the printing when fine halftones are used. Another simple test is to examine the coating visually with a light source behind the sheet. This will show up (as a result of the difference in the amount of light transmitted) any imperfections which are important enough to cause trouble in printing.

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[191] A. E. Hughes and H. F. Roderick, *Paper Trade J. 110*, No. 26: 347 (June 27, 1940)

[192] E. Sutermeister, *Paper Mill News 64*, No. 25: 76, 78 (June 21, 1941)

A number of defects commonly occur in coated papers. Papers coated with casein or soybean protein often contain pinholes caused by foam in the coating mixture. Pinholes are caused by foam which does not break until the coating is partially dried and is no longer fluid enough to fill the hole left by the ruptured bubble. This leaves small pits in the dried coating which vary from almost invisible spots up to pits which are 0.064 mm. in diameter.[192]

Another type of surface irregularity is that caused by improper application and smoothing of the coating. In brush-coated papers, improper flow results in the presence of brush marks. In roll-coated papers, imperfections in the form of ribs or ridges often occur. The frequency and size of these ribs are determined by the surface tension of the coating mixture and the size of the coating roll; in some cases, a smaller smoothing roll is placed after the larger coating roll in order to reduce the ribbed effect. At about 75 to 80 ridges per inch, the eye can no longer perceive these irregularities,[193] but even so, they still interfere with the reproduction of halftones made from screens containing 100 or more lines per inch. Machine-coated papers are likely to have surface imperfections, due to scratching of the coating on the drier rolls.

Other conditions which may result in imperfections in the surface of coated papers are the presence of loose fibers, dirt, or other extraneous material in the coating mixture. Starches which contain fine filaments of nylon originating from the nylon reels used in screening the starch have even been reported as causing trouble. Cotton fibers cause less trouble because they take printing ink more readily than nylon. Particles of undispersed adhesive or pigment in the coating have also been known to cause trouble. Undispersed pigment particles produce lumps in the dried coating, whereas adhesive particles tend to produce depressions caused by a drying-out and contraction of the adhesive. The latter condition may produce pits which are somewhat similar to foam spots, but which can be distiguished from foam spots by their irregular shape. Either starch or casein coatings may contain these pits if the adhesive is not properly dispersed. In addition, certain starches may contain undispersed fragments of starch granules which tend to produce very small pits in the coating,[194] as shown in Figure

[193] J. F. Halladay, *Modern Packaging 17,* No. 10: 111–115, 140, 142 (June, 1944)
[194] J. P. Casey, *Paper Ind. 26,* No. 2: 157–162 (May, 1944)

XVIII-24. Pits produced in this way are barely visible with a hand lens magnifying 20 times, and consequently do not cause trouble except possibly on the finest printing jobs.

Oil emulsified in the coating mixture will cause trouble by forming oil spots in the coating. Oil which has leaked into the coating from the bearings on the mixing tanks forms an unstable emulsion which is broken during the drying process, thereby producing oil spots. Excessive amounts of added oil (e.g., pine oil or sulfonated oils) will sometimes produce a similar condition. Oil spots in paper show up by fluorescing under ultraviolet light.

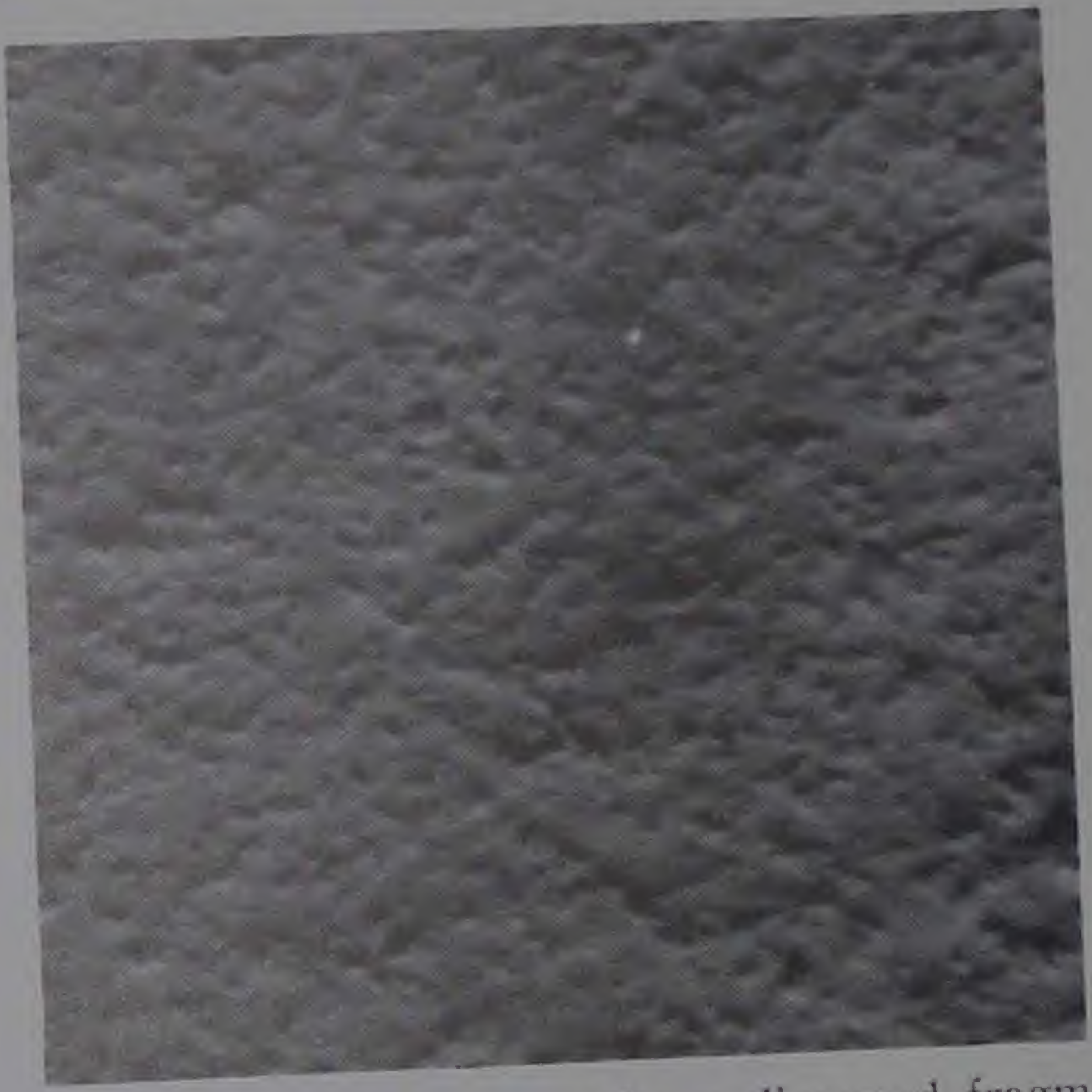

Fig. XVIII-24. Pits in coating caused by undispersed fragments of starch.

Coated papers (except cast coated) are not smooth until calendered, so that the smoothness of the coating depends primarily upon the ease with which the coating can be calendered. There is considerable difference in the ease of calendering, depending upon the amount of adhesive in the coating and the type of pigment used. Landes[188] points out that the smoothness obtained passes through a maximum as the ratio of adhesive to pigment in the coating formula is increased. However, after the point of maximum smoothness is reached, the smoothness decreases with increasing adhesive, and consequently coated papers which contain an excess of adhesive are generally less smooth than those with a normal amount of adhesive. The decrease in smoothness which occurs when high percentages of adhesive are used is caused by a reduction in the plasticity of the coating which causes it to calender less readily. The type of pigment and the pigment particle size are other important factors. Satin white, titanium dioxide, clay, calcium carbonate, and lithopone tend to produce coatings of high smoothness. Clay-coated sheets are generally increased in smoothness by calendering more than calcium carbonate coated sheets because of their greater plasticity. The other factors affecting the calendering operation have already been discussed.

Gloss

Gloss is a measure of optical smoothness. In the early production of coated papers, an attempt was made to obtain the highest possible gloss, but today it is realized that high gloss is not required in all printing papers. Excessive gloss is disturbing to the reader. A matte or dull-finished paper makes the best reading surface, even though the paper does not print quite so well as a highly finished paper. Coated papers for printing should have high brightness and smoothness, but not show glare when illuminated by light at high angles. It is quite possible to prepare a sheet with the best possible printing qualities and still avoid gloss, although all printers will not agree with this statement. For this reason, some specular gloss is desirable from the sales standpoint.

The amount of calendering is the most important factor affecting gloss. Some pigments calender to a higher gloss than others, and in this respect, satin white and certain clays excel. The finer clays produce glossier coatings than the coarse clays. Titanium dioxide is considered a high finishing pigment. On the other hand, calcium carbonate and blanc fixe are considered dull finishing, since they calender to a lower gloss Water-ground calcium carbonate produces a lower gloss than the precipitated grade. It is possible to control the gloss independently of the brightness through proper choice of pigment.

In general, the gloss of the coating decreases as the adhesive-to-pigment ratio is increased. In some cases, however, the adhesive increases the light-deflecting surface and increases the glare. Ordinarily, starch-coated papers do not calender with as much gloss as casein-coated papers. On the other hand, glue-coated paper gives a comparatively high gloss, and glue is sometimes used as the adhesive when maximum gloss is desirable. Latices, which are thermoplastic, are conducive to the production of highly finished coatings.

Brightness and Opacity

Most coated papers are printed or used for their decorative effect, and consequently the optical properties of the coating (brightness, color, and opacity) are highly important. A paper with a white, bright surface is desired, and these properties are derived from the coating layer. In the ideal coated paper, the optical properties would be primarily those of the coating and not those of the raw stock.

In order for the coating layer to fulfill its functions, it must (*1*) cover up the base paper through the effect of the opacity or hiding power of the pigment and (*2*) present a white, bright surface obtained through the natural brightness of the pigment. A coating which is deficient in either hiding power or brightness will not be satisfactory. For example, a white, translucent coating would be unsatisfactory because it would not cover up the base paper. Likewise, an opaque, colored coating would be undesirable because of its low brightness.

If the base paper is low in brightness and the amount of applied coating is small, the hiding or opacifying power of the pigment is a more important factor than the brightness of the pigment. Under these circumstances, pigments of high hiding power produce brighter coatings than pigments of low hiding power if the brightness of the pigments is the same (or even if the brightness of the pigment of high hiding power is slightly the lesser of the two). On the other hand, when the amount of applied coating is large, the hiding power of the pigment becomes secondary to the brightness of the pigment. Stated differently, it is better to have a pigment which will cover up the body stock rather than a pigment which has a high natural brightness of its own when low coat weights are applied. When heavy coat weights are applied, it is better to have a pigment of high brightness, rather than high covering power, because the pigment so completely obscures the body stock that the brightness of the coated paper is essentially the brightness of the coating. Pigments of high covering power are always desirable because they produce the desired opacity at lower coat weights than pigments of low covering power.

In commercial coating, the coat weight is generally less than that required to obscure completely the body stock, and consequently the hiding power of the pigment is highly important. The coat weight necessary with clay coatings to obtain complete coverage of the raw stock, i.e., enough coverage so that additional coat weight has no further effect on the brightness, varies from 14 to 50 lb., depending upon the particle size distribution of the clay[195] (see Fig. XVIII-22). The effects of coat weight and pigment composition on the brightness of coated paper are shown in Figure XVIII-25 for two raw stocks of different brightnesses.[196] The pigment composition was 100% calcium carbonate in one case and 70% calcium carbonate and 30% titanium dioxide in the other. The titanium dioxide and the calcium carbonate had approximately the same brightness, but of course the hiding power of the titanium dioxide is higher than that of calcium carbonate. It can be seen from Figure XVIII-25 that the brightness of the raw stock is an important factor at low coat weights, and is more of a factor when pigments of low covering power (e.g., calcium carbonate) are used than when a pigment mixture of high covering power (mixture of calcium carbonate and titanium dioxide) is used. Somewhat similar data are presented in Table XIII,[197] showing the effect of raw stock brightness and coat weight on the brightness of coated paper when a 100% clay coating is compared with a coating containing 90% clay plus 10% titanium dioxide.[197] Because of the great hiding power of titanium dioxide, a 5-lb. coating containing 90% clay and 10% titanium dioxide has approximately the same brightness as a 10-lb. coating containing 100% clay.[198] If ti-

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[195] O. W. Callighan and C. G. Albert, *Year Book*, Am. Pulp Paper Mill Supts. Assoc. 1945: 184, 186, 188, 190, 192, 194, 196, 198, 200

[196] TAPPI Monograph No. 7, "Pigments for Paper Coating," p. 3, Tech. Assoc. of Pulp & Paper Ind., New York, N. Y. (1948)

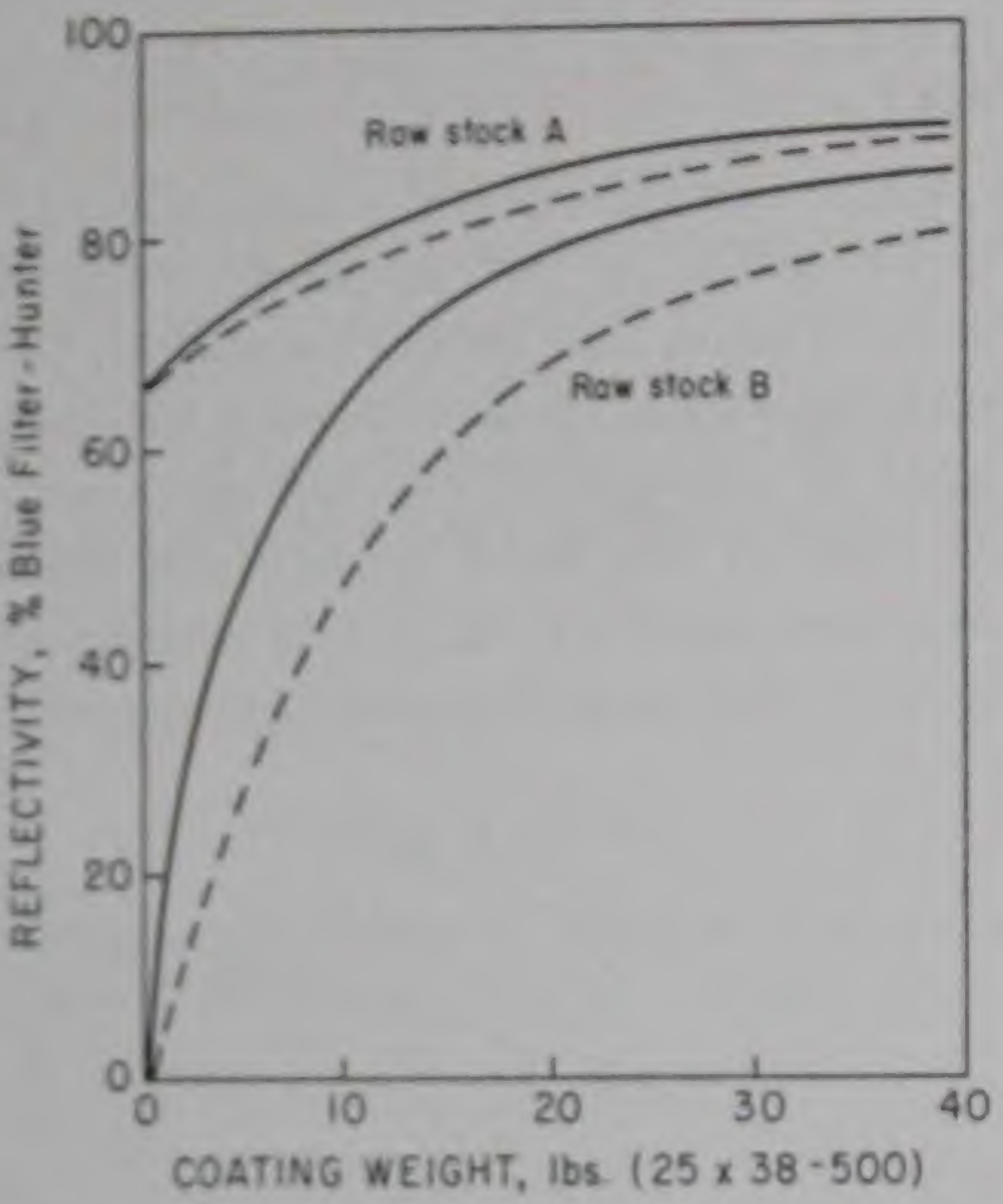

Fig. XVIII-25. Effect of coat weight and pigment composition on the brightness of coated paper. (—) 70% calcium carbonate and 30% titanium dioxide; (- - -) 100% calcium carbonate.

TABLE XIII

Effect of Raw Stock Brightness and Coat Weight on Brightness of Coated Paper

Reflectivity, %

Raw stock brightness:	74.0		77.5		80.0	
coat weight lb., 25 x 40—500	All clay	10% TiO_2	All clay	10% TiO_2	All clay	10% TiO_2
5	77.0	79.0	80.0	82.0	82.0	83.5
10	79.5	83.0	81.5	85.0	83.5	86.0
15	81.0	85.0	82.5	86.0	84.0	87.0
20	82.0	86.0	83.0	86.0	84.5	87.5

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[197] *The Handbook*, Titanium Pigment Corporation Subsidiary, National Lead Co., 111 Broadway, New York, N. Y.

[198] W. R. Willets, *Paper Ind. 28*, No. 10: 1458–1460 (Jan., 1947)

tanium pigments are substituted for part or all of the clay, the coating will have a higher brightness, but heavier coat weights may be required to obtain the ultimate brightness and covering power.[199] Satin white has less hiding power than clay, whereas calcium carbonate has slightly more hiding power than clay.

The over-all opacity of coated paper is determined by the opacity of the coating layer plus the opacity of the raw stock. The coating layer is the more important factor if heavy coat weight or coatings of high hiding power are used, whereas the opacity of the raw stock is the more important factor if light coat weights or coatings of low hiding power are used. Table XIV[200] shows the effect of raw stock opacity and coating weight on the over-all opacity of coated paper; a 100% clay coating is compared with a coating containing 90% clay plus 10% titanium dioxide.

TABLE XIV

EFFECT OF RAW STOCK OPACITY AND COAT WEIGHT ON OVER-ALL OPACITY OF COATED PAPER

Contrast ratio, Bausch and Lomb, %

Raw stock opacity:	58.0		66.0		76.5		85.0	
coat weight, lb., 25 × 40—500	All clay	10% TiO_2	All clay	10% TiO_2	All clay	10% TiO_2	All clay	10% TiO_2
5	69.0	74.0	74.0	78.0	82.0	84.5	88.0	90.0
10	78.0	84.0	81.0	86.0	87.0	90.5	90.5	93.5
15	84.0	89.5	86.0	90.5	90.0	93.5	92.5	95.0
20	87.0	92.0	88.5	93.0	92.0	95.0	93.5	96.0

As mentioned above, an ideal coating pigment should have both high brightness and good covering power. Brightness is determined principally by the natural brightness of the pigment and the particle size distribution. Some of the pigments which have a naturally high brightness are calcium carbonate, titanium dioxide, and satin white. Clay, lithopone, and blanc fixe have a lower brightness, clay generally having the lowest brightness of all. The brightness of coated papers made from different pigments is shown in Figure XVIII-26.[191] However, in interpreting these data, it should be remembered that the various pigments have unequal adhesive demands (see Fig. XVIII-16), and hence, the brightness obtained on coated papers of equal strength would be quite different from the values indicated in Figure XVIII-26.

Hiding power of the pigment is determined by the index of refraction and the particle size distribution. The optimum average particle size and particle size distribution for coating pigments have not been accurately determined, but it is known that the presence of pigment particles appreciably less than 0.25 micron in size tends to decrease the brightness of the coating.[201, 202] Calcium carbonate pigments containing a high percentage of particles less than 0.2 micron in diameter produce a dull gray coating.[201] A particle size between 0.5 to 1.0 micron is considered optimum for clay from the standpoint of hiding power. Since coating clays do not differ appreciably in their refractive index, the relative hiding power of clays is primarily a function of their particle size. An important consideration, as mentioned above, is the percentage of clay particle within the range of 0.5 to 1.0 micron, since these are the particles having the greatest opacifying effect. Pigment flocculation in the coating reduces opacity by reducing the probability of light striking a pigment particle. The effect which is obtained is shown schematically in Figure XVIII-27 where it can be seen that the coating containing flocculated pigment permits the passage of more light than the coating containing deflocculated pigment. Some of the pigments which are associated with good hiding power are calcium carbonate, titanium dioxide, satin white, and zinc sulfide. The effect of different pigments on opacity of coated paper is shown in Figure XVIII-28.[191] When comparing pigments for opacifying effect, all comparisons should be made on coatings of equal brightness, since the opacity increases with decreasing brightness. With high brightness pigments such as titanium, it is possible to obtain additional opacifying effects by reducing the brightness with dulling agents.

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[199] W. R. Willets, *Tappi 32,* No. 8: 349–356 (Aug., 1949)

[200] Taken from *The Handbook,* Titanium Pigment Subsidiary, National Lead Co., New York, N. Y.

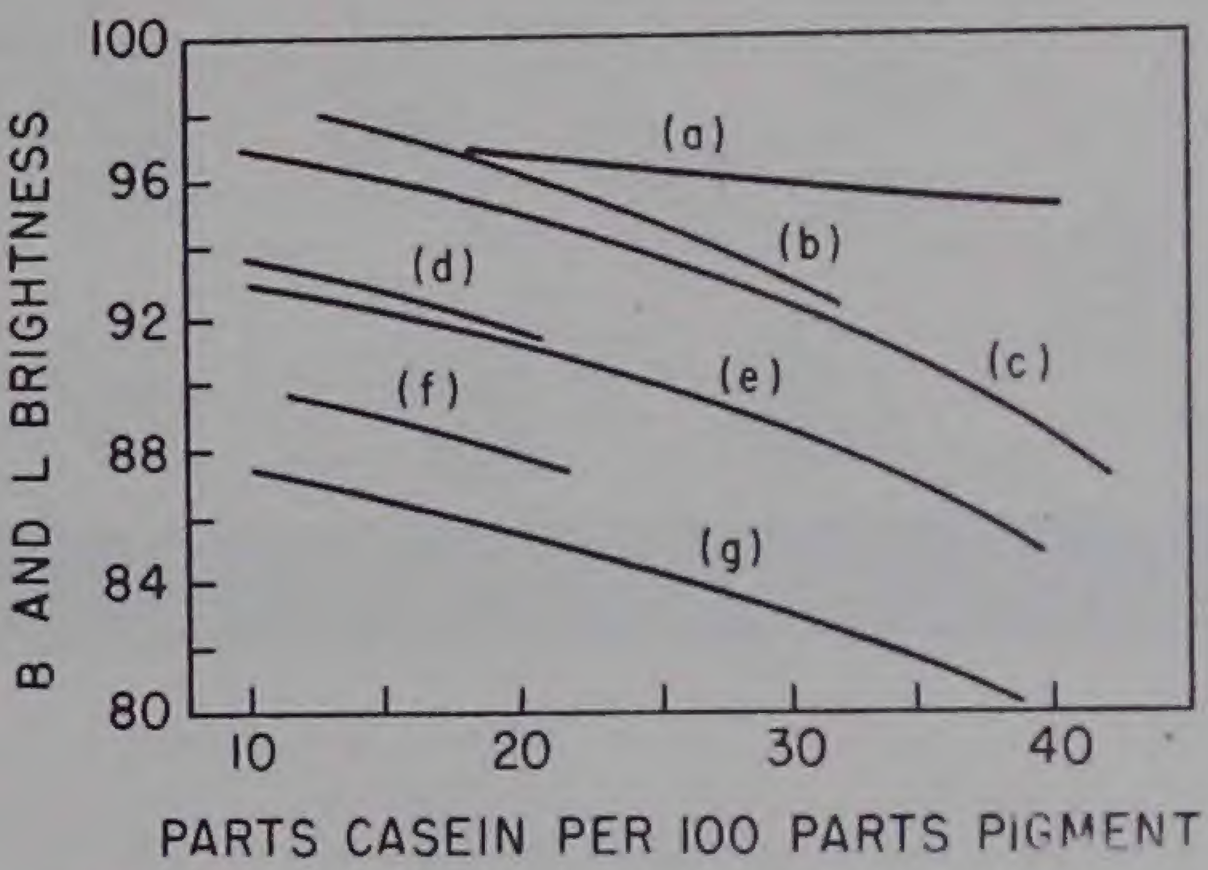

Fig. XVIII-26. Effect of different pigments on brightness of coated paper.[191] (a) Satin white, (b) titanium dioxide, (c) calcium carbonate, (d) lithopone, (e) English clay, (f) blanc fixe, and (g) domestic clay.

The opacity of the coating layer depends upon the difference in the refractive indices and the relative proportion of the various components in the coating, including air, pigment, and adhesive. The greatest difference in refractive index is between the air and pigment. Thus, increasing the amount of adhesive in the coating reduces the opacity because air is being replaced by adhesive (see Fig. XVIII-28). Increasing the degree of calendering decreases the opacity because it reduces the proportion of air.

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[201] A. R. Lukens, C. G. Landes and T. G. Rochow, *Paper Trade J. 112*, No. 15: 183–190 (Apr. 10, 1941)

[202] G. F. A. Stutz, *J. Franklin Inst. 210*, No. 1: 67–85 (July, 1930)

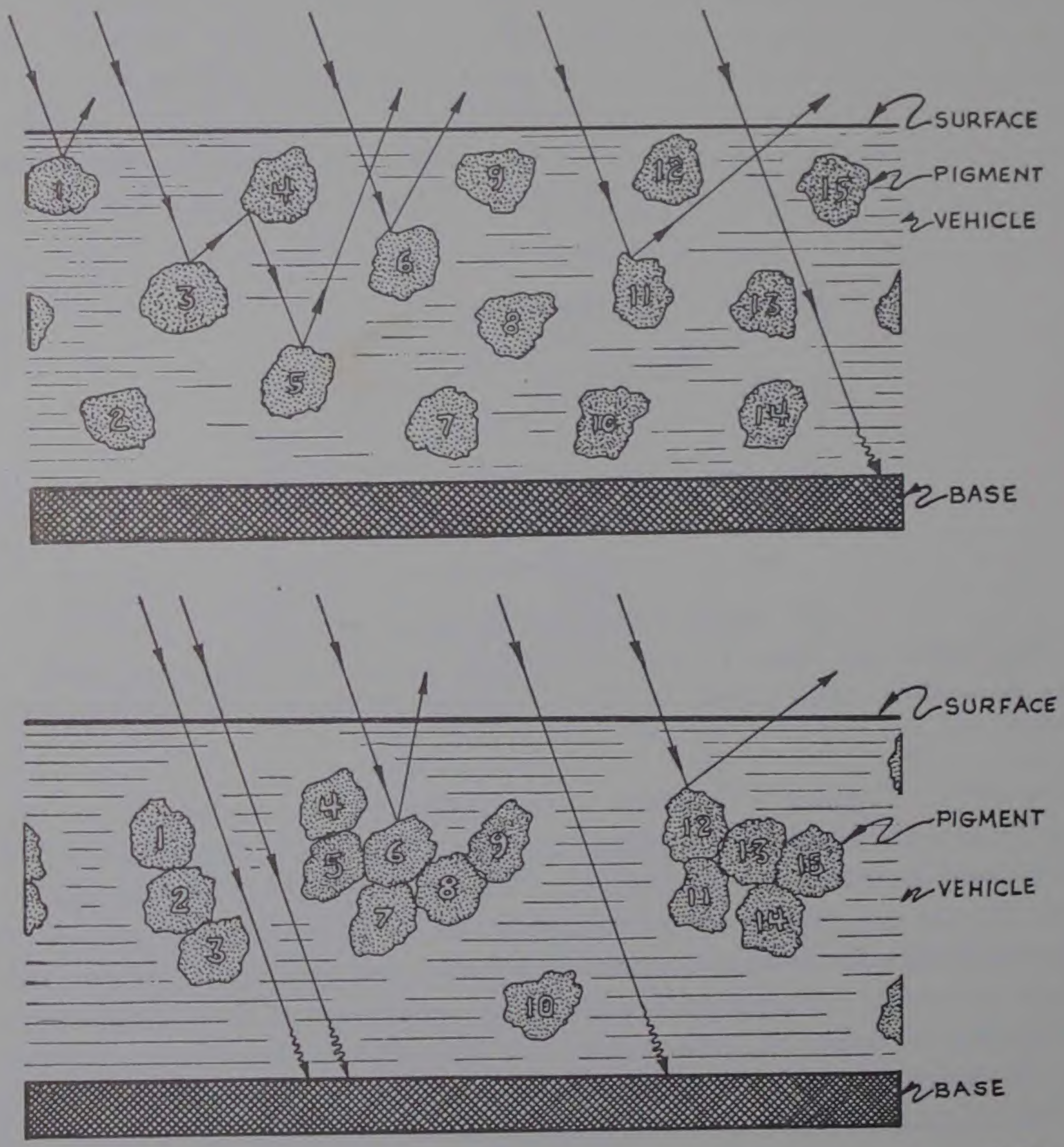

Fig. XVIII-27. Showing how flocculation affects the transmission of light through pigment coatings. Top figure, light entering deflocculated system. Lower figure, light entering a flocculated system (courtesy Interchemical Corp.).

The brightness is reduced with increasing adhesive (see Fig. XVIII-26) because the brightness of the adhesive is less than that of the pigment, and also because the adhesive is fairly transparent and hence reduces the total amount of light reflected and refracted. Starch generally reduces brightness and opacity somewhat less than an equal amount of casein or soybean protein because of the slightly higher brightness of starch.

However, from a practical standpoint, less casein than starch is required to obtain a coating of the same strength, and consequently, casein-coated papers are usually higher in brightness than starch-coated papers at equal strengths. Starches differ slightly in color, but generally there is not enough difference in color between starches to make any significant difference in the color of the coating, although some of the more highly modified dextrins may produce slightly dull coatings. Soybean protein produces coatings of slightly poorer color than casein.

The principal means of regulating the brightness and opacity of coated paper is by changes in the pigment formulation. Other means of changing these optical properties are generally fixed by other requirements of the paper. For example, the amount of adhesive used is determined by the strength requirements, rather than by the brightness and opacity requirements. In the same manner, the coat weight is determined by cost, basis weight, and printing requirements, rather than by opacity and brightness values.

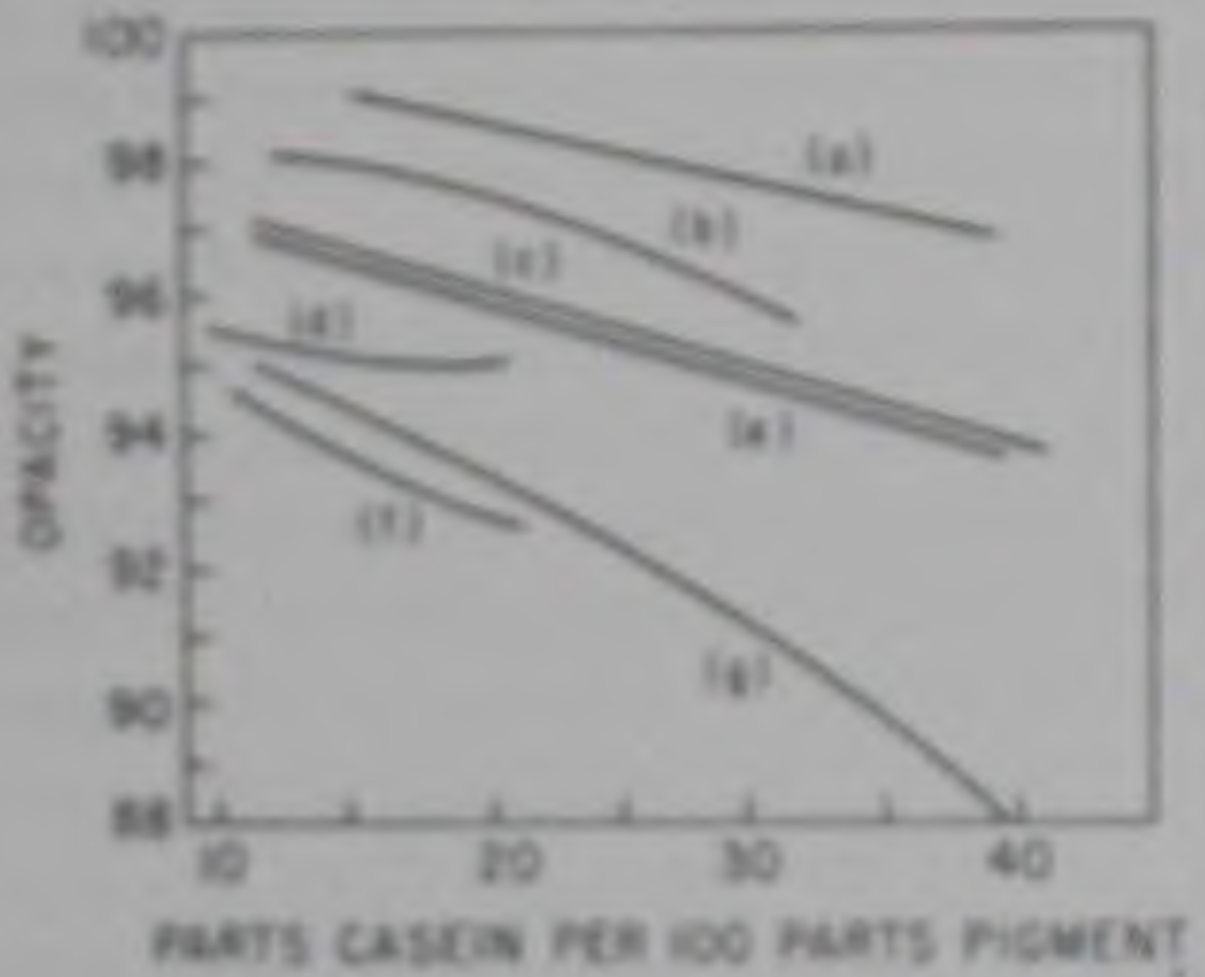

Fig. XVIII-28. Effect of different pigments on opacity.[195] (a) Satin white, (b) titanium dioxide, (c) calcium carbonate, (d) lithopone, (e) English clay, (f) blanc fixe, and (g) domestic clay.

Special Coating Processes

Up to this point, most of the discussion has been limited to methods for the preparation of the standard grades of coated papers, such as coated book and coated magazine papers. There are, however, a number of grades of coated papers which require special formulations and special techniques. A few of these are discussed in the following sections.

Wallpaper Coating

Wallpaper coating differs in several respects from the coating of such grades as book and magazine papers. For one thing, wallpaper is coated in two stages. In the first stage, a base or ground coating is applied which consists of clay and a binder, such as casein, animal glue, starch, soybean protein, soy flour, or gum arabic. In the second stage, a top coating in colored designs or patterns is printed upon the ground coating.

Gum arabic (Egyptian gum) was one of the earliest adhesives used in wallpaper coating. This gum is obtained from the Anglo-Egyptian Sudan, where it is produced as an exudation of a tree (acacia verek) which grows in a semi-wild state. The gum is formed beneath the bark during the rainy season and collected in November by tapping the tree. The first gatherings are light in color, and the later gatherings are darker. The gum must be aged, and for the high-quality grades, must be cleaned and processed. In modern wallpaper coating, gum arabic has been replaced almost entirely by other adhesives. Animal glue, casein, soy flour, soybean protein, and synthetic resin latices are the principal adhesives used in the production of washable or water-fast wallpaper, whereas starch is used in the non-washable grades. The washable grades can be washed with soap and water without disturbing the coating. Very little wallpaper is actually washed by the housewife, but washable paper is useful in cases where the wall becomes spotted, and it also helps the paperhanger who may have to remove paste spilled on the paper. Casein makes the most highly washable paper, with soybean protein next, and animal glue last. Finely ground soy flour may be used in making washable wallpaper in the proportion of 25 to 50% of the total adhesive demand if the remaining adhesive is some other protein, such as casein or soybean protein. Soy flour has also been used as the entire adhesive with fairly good results, but a higher percentage of adhesive on the weight of the clay is required. If soy flour is used, the flour should be ground so that 98 to 99% passes a 270-mesh wire, since particles which are much larger than the openings in a 200-mesh sieve will not pass through the nip of the roll running against the paper, and consequently these particles tend to accumulate in the coating mixture.[203]

The first, or ground, coating is used in wallpaper manufacture to furnish a proper background for the top coating and to make the finished paper fast to light by covering up the yellowing of the groundwood. This coating is similar to regular paper coating except that less adhesive is used in the coating formula and, as a result, the coatings are much weaker. Ordinarily, between 5 to 10% of adhesive on the weight of clay is sufficient for the ground coating. Coarse grades of clay are used compared with the clays used in the coating of magazine papers, because a rough, matte surface is desirable. Only rarely, if at all, are the more expensive pigments used, such as calcium carbonate or titanium idoxide. Clays of 80 to 81% brightness are adequate for most ground coatings. Ground coating is not calendered, but is used as a base for the colored coating, which is subsequently applied in the second operation. A typical ground coating for washable wallpaper is: 100 parts medium-grade clay, 7 parts casein, 135 parts water, 0.3 parts pine oil. The casein is dispersed with alkalies in the usual manner. Then, enough casein solution is added to the clay slurry to give about 7% casein on the weight of the clay (dry basis). The ground coating can be applied by brush, air knife, or roll coaters. The coated paper is then dried and is ready for the top colors to be applied in the proper design. About 14 to 22 lb. of ground coating are applied per ream (24 × 36—480).

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[203] G. Davidson and J. H. Cagle, *Paper Ind. 29*, No. 3: 364–366 (June, 1947)

The top colors (sometimes called "stainers" or "toppers") are applied by a special coating machine consisting of a series of printing rolls arranged around the periphery of a large drum about which the paper is wrapped. Each printing roll applies a different color to the paper in the proper sequence and proper register to produce the required design on the paper. The colors are similar to the ground coating, except that higher adhesive-to-pigment ratios are used, generally a total of 8 to 14% adhesive on the weight of the pigment—and finer clays are often used. Colored pigments or lakes are added to the coating mixture to obtain the desired colors. As many as fifteen to twenty different top colors may be required for a single printing although generally eight to thirteen are used. Printing is done either from aluminum alloy rolls or from wooden rolls covered with pieces of felt which are held in the proper place by brass strips. The printing rolls receive the color by means of a felt sleeve, known as a sieve cloth, which receives color from an individual color pan. Special coating mixtures are often used in the top colors, e.g., coatings containing 100% titanium dioxide are sometimes used for the highlights. The top colors must have a higher viscosity than the ground coating mixture in order to pick up properly on the printing rolls.

A third operation is carried out in making the washable grades of wallpaper. This consists of treating the surface of the coated paper with a solution of hardening agent, i.e., formaldehyde or alum solution, to harden the coating and make it water-resistant. Formaldehyde is not widely used as a hardening agent because of its disagreeable odor; alum is used almost exclusively, even though it has the disadvantage of reducing the flexibility and permanence of the paper. A typical hardening solution used for treating washable papers is: 20 lb. papermaker's alum, 10 lb. sodium acetate, 50 gal. water. The function of the alum is to coagulate or reduce the solubility of the protein adhesive in the coating so that the coating can be washed with a wet rag without removing the coating. The aluminum ion is the agent mainly responsible for the hardening effect, and other aluminum salts work about as well as alum. Starch-coated papers are not treated because they cannot be made water-resistant by this method. After the hardening solution is applied, the paper is dried in either flat-bed or festoon type driers, hot air ducts being used to aid in drying. The finished paper is then wound into rolls.

The raw stock used for wallpaper is a grade of paper known as hanging stock. It is made principally of groundwood, together with enough sulfite (usually about 15 to 20%) or other long-fibered stock to give the paper enough strength to pass trough the coating machine and the drying operation. The only significant difference between hanging stock and newsprint is the greater weight, higher percentage of sulfite stock, and the greater amount of rosin sizing (1 to 2½% rosin size) in hanging stock. Some wet strength is desirable, and the paper must have considerable stretch when wet so that the wallpaper hanger can match patterns even though there are large irregularities in the wall.

Another grade of raw stock called No. 1 Hanging is used in small amounts for the more expensive wallpapers. It is usually made from bleached soda and sulfite pulps. All hanging stock is lightly calendered, since a bulky sheet with a rough, toothy surface is desired. Hanging stock is generally sold in weights of 38, 42, 50, 58, 66, 74, 82, and 98 lb. on the basis of a ream size of 24 × 36—480. The finished wallpaper is sold by rolls (width 20 in. and length 9 yd.). The weights of the hanging stock listed above are frequently designated in the trade as 9, 10, 12, 14, 16, 18, 20, and 24 oz., respectively, on the assumption that raw stock of the given weight in pounds will result in a roll of wallpaper of standard length and width weighting the corresponding ounces.

There are very few tests made on the finished wallpaper. The wax pick test is rarely used, principally because the coating is so weak. One crude test which is commonly made consists of rubbing the ground coating 10 to 50 times with a small piece of paper, and then visually examining the surface of the paper for the amount of coating removed. A good coating should produce very little dust under these conditions; otherwise, the percentage of adhesive in the ground coating mixture should be increased.

A good grade of washable paper should withstand at least 25 to 100 rubs when wet with water and rubbed with a special device consisting of a rubber sponge covered with cloth gauze and weighted with a 4-lb. weight.[204] A dilute soap solution is used to wet the paper, and generally the paper will withstand more rubs in this medium than in pure water. Ordinarily, the rub test is carried out immediately after the coated paper is taken from the machine, but the washability tends to improve slightly on aging for a period of about one month, after which time it remains fairly constant.

Varnished Papers

Some grades of coated paper, such as certain grades of wallpaper, label paper, and playing cards, are given a coating with clear spirit varnish in order to increase the luster and durability of the surface. This is known as varnishing, and is discussed further in the chapter on protective coating. Varnished papers are generally coated with pigment before varnishing in order to provide a better surface for printing. The various steps include coating the paper with pigment to improve the printing qualities, printing the paper, and finally varnishing to improve the appearance and increase the durability. The pigmented coating not only provides a better printing surface, but also reduces the consumption of varnish by reducing penetration of varnish into the paper.

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[204] Test devised by United Wall Paper, Chicago, Illinois

Coated papers for varnishing are made in the same manner as regular coated papers. There are, however, several important differences. Ordinary coated papers are not satisfactory for varnishing because they are too absorbent and cause the varnish to strike into the coating. In preparing coated papers for varnishing, the type of pigment and adhesive, and the ratio of adhesive to pigment are factors to be considered. The finer the pigment and the greater the filming properties of the adhesive, the greater the varnish resistance. Table XV shows the amount of different adhesives which are required in order to obtain a coated sheet of good varnish resistance, using two different clays, with average particle size of 1 and 5 microns.[205]

TABLE XV

AMOUNT OF ADHESIVE REQUIRED IN COATED PAPERS FOR VARNISHING FOR CLAYS OF DIFFERENT PARTICLE SIZE[205]

Average particle size of clay, microns	Adhesive required in coating based on clay		
	Casein, %	Animal glue, %	Starch, %
5	30	40	60
1	16–18	22	24–30

It is apparent from Table XV that higher percentages of adhesive are required for coated varnishing papers than for regular coated papers. The percentage of adhesive required is greater the larger the average particle size of the pigment. In the matter of different adhesives, it is evident that starch is the poorest and casein the best. Alkaline coatings seem to resist varnish better than acid coatings; the presence of about ½% of soap in the coating is sometimes helpful.[205] After coating, the paper should be calendered at high moisture content (e.g., 4%) in order to obtain the highest possible gloss. The raw stock is an important part of coated papers for varnishing. The raw stock for coated varnish papers should have approximately the same properties as uncoated varnish papers. In particular, high density is important.

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[205] Private communication to the author from N. I. Bearse, Champion International Paper Company

Tests made on coated papers for varnishing are the same as those made on regular coated papers. The wax pick test is much higher, occasionally being over a Dennison wax of 10. If the paper is to be covered with solid printing before varnishing, there is no need for special varnishing properties, since the printing ink will provide a satsfactory base for the varnish. If, however, the paper is to be printed in only a small area, the varnishing properties are important. The best method of testing coated varnishing paper is by applying a film of spirit varnish to the paper by means of a laboratory coater and then comparing the results with a standard paper for gloss, discoloration, and loss of opacity.

Opaque Bread Wrap

Paper for opaque bread wrap is coated with pigment to offset the loss in opacity which would otherwise result on waxing. In this application, a pigment with a very high index of refraction is required. Clay is practically valueless so far as increasing the opacity after waxing is concerned because of its low index of refraction. Either 100% mixed titanium pigment (30% rutile titanium dioxide and 70% calcium sulfate) or 30 to 40% pure titanium dioxide and 60 to 70% clay are commonly used as the pigment in coated opaque bread wrap. Paper coated with titanium pigment loses opacity on waxing, but the loss is not as great as that which occurs with clay-coated paper. For example, Willets[206] has shown that the opacity decreases from 70 to 24% on waxing 100% clay-coated paper, whereas the opacity decreases from 72 to 42% upon waxing a coated paper containing 25% titanium calcium pigment and 75% clay, based upon a 6-lb. coating (containing 25% starch adhesive) applied to 25-lb. raw stock.

Greater amounts of adhesive are generally used in coatings for opaque bread wrap than in ordinary grades of coated paper in order that the coating will not absorb too much wax. One interesting point here is that the high amount of adhesive used in these papers is not harmful to brightness and opacity (unlike unwaxed papers), because wax and adhesive have about the same refractive index, and thus it makes little difference whether adhesive or wax is present in the coating so far as brightness and opacity of the paper are concerned. A suitable formula for coated bread wrap is: 100 parts mixed titanium pigment, 30 to 40 parts starch, 200 to 260 parts water. The coating is frequently applied on a large Yankee drier.

Coated Flour Bags

Another special grade of coated paper is that used for making flour bags for the retail market. The familiar blue and white flour bag is generally coated on the outside with a coating similar to a regular casein-clay coating, except that more adhesive is used in the coating formula. A high strength is required in this grade of paper in order to resist the picking action of the exceedingly tacky inks used in printing. Starch-coated papers have not been satisfactory because the high percentage of starch required tends to dull the coating.

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[206] W. R. Willets, *Tappi 32,* No. 8: 349–356 (Aug., 1949)

Sandpaper

Sandpaper is a special type of coated paper which is quite different from the grades of coated papers already discussed. In the process of making sandpaper, grains of abrasive such as flint, garnet, silicon carbide, or emery are bound to the base paper with an adhesive made from animal glue or a synthetic resin. Synthetic resins such as the alkyds and phenolic resins are used as the adhesive when the paper is to be used for wet sanding in water, whereas animal glue is used for regular paper for dry sanding. Hide glue is used because of its higher strength compared to bone glue.

Bleached and unbleached kraft pulps and rag stock are the common pulps used in the manufacture of abrasive papers. In some of the best grades, manila hemp may be used. Wet-strength paper is used for the wet sanding grades and ordinary paper for the dry sanding grades. In some cases, the paper may be impregnated with paraffin or linseed oil and then coated with a resin dissolved in linseed oil, which acts as the binder. The paper is usually quite heavy, ranging from 40 to 90 lb. for hand sanding grades to 130 lb. for mechanical sanding grades (24 × 36—480). Fourdrinier papers are used for hand sanding grades and cylinder papers sometimes used for mechanical sanding grades.

In the coating process, a layer of adhesive is first applied to the paper, and then grains of abrasive are dropped as evenly as possible on the wet adhesive film. Then, an anchoring coat of adhesive is applied over the abrasive to hold the individual grains more firmly. It is necessary that the abrasive particles be well wetted by the binder to obtain the maximum bonding effect. In recent years, a new method of distributing the abrasive has been developed which uses an electric field of about 40,000 to 50,000 volts between the drive belt carrying the grains of abrasive and the glue-coated paper held about ¾ in. away. As the grains enter the electric field, they are picked up and transferred to the paper. The electric field lines up the particles of abrasive in the direction of their long axis, and since they all have the same charge, they are kept in uniform distribution over the surface of the paper.

Specialty Coated Papers

A number of specialty coated papers are used for making fancy greeting cards, tags, labels, menus, match boxes, wrappings, and similar special items. This field of paper coating is highly specialized, and many types of products are made for small special uses. Among the most important grades are mica coated papers, metallic coated papers, flock coated (velour) papers, and luminescent papers.

Mica coated papers are made by coating the paper with an adhesive, and then while the adhesive is still wet, adding finely ground mica. Metallic coated papers are made by dusting fine metal powders on the surface of freshly coated paper or by mixing finely ground metal powders (e.g., gold, copper, or aluminum) or metal oxides with a suitable adhesive and then coating the mixture on the paper. If metal oxides are used, it is customary to burnish the coating on a friction calender or on a brushing machine.

Flock coated papers are made by dusting the freshly coated adhesive surface while the adhesive is still wet with fine flock made from cotton, wool, rayon, silk, or animal fiber. An electrostatic device is used to cause orientation of the fiber.

Luminescent papers are made by coating the paper with a mixture of adhesive and appropriate luminescent pigments (see section on luminescent pigments in this chapter).

CHAPTER XIX

PRINTING

Approximately 90% of all paper is printed by some means or other. Many grades of paper are made primarily as a base for the printing. In these grades, the printability of the paper is the most important property, although strength and other physical properties of the paper must be adequate to meet the functional requirements.

Printing is a complex colloidal phenomenon. It involves the application of a liquid or plastic material (the printing ink) to a colloidal fibrous membrane (the paper) under conditions of high speeds, with the object of producing certain optical effects on the printed paper. Slight variation in printing ink, paper, or press conditions can throw the system out of balance.

The paper chemist is primarily interested in the quality of the paper, but in order to form an able opinion of its printing qualities, it is necessary that he understand the basic steps in the printing operation, complex and variable as they are. Unless the papermaker possesses this knowledge, he can never be certain that the paper is properly used. Paper cannot be changed after it has reached the printer, and consequently any major adjustments made at the time of printing must be made in the ink or in the press conditions. The only recourse which the printer has when he considers the paper at fault is rejection of the order. To be certain that the paper is not rejected unfairly when the ink or pressroom conditions are at fault (or at least unsuited to the paper), the paper chemist must be familiar with the properties of printing inks, the conditions of pressroom operation, and some of the common remedies which the pressman is likely to use, many of which may be unsuited to the paper. The proper paper for a given printing depends upon the type of printing press on which the paper is to be printed, the type of printing process, and the type and method of drying the ink. The printer should likewise make an effort to learn more about the properties of paper. Cooperation is the keynote, and although there is much more of this than formerly existed, the printer and the papermaker can profitably learn more about each other's problems.

Printing is an old process, having been used by the Chinese as early as the eighth century. The industry was given a great impetus by the introduction, about 1450, of movable type, the invention of which is generally attributed to Gutenberg. Other significant developments came later, such as the development of photoengraving in England in 1852, and later on, the invention by Ives of the halftone process, which for the first time made it possible to obtain tone gradations in printed illustrations. The development of pigment-coated papers was another important step, because it made possible papers of very high surface smoothness which were particularly well adapted to halftone printing.

Printing Processes

There are three principal printing processes: relief, planographic, and intaglio. In the relief process, sometimes called the letterpress or typographic process, the ink is held on a raised printing surface. In the planographic process, usually called the lithographic or offset process, the ink is held on a plane surface. In the intaglio process, called the photogravure or rotogravure process, the ink is held by recesses in the plate surface.

Relief or typographic is the oldest form of printing, and more printing is done by this process than any other. Planographic or lithographic printing was not developed until about 1798, but did not have a very wide use until the offset press was developed about 1906. Since that time, offset lithography has increased rapidly and is still expanding in use. Offset has not replaced relief printing, but has increased the total amount of printing paper used. Intaglio printing is important for certain types of printing; its greatest use is in rotogravure. Another printing process is silk-screen printing, which is a fast growing process for short runs on special multicolor printing. Collotype and photogelatine printing are special printing processes classed with lithography, since they are a water-ink process. They may be handled as direct or offset lithography.

With the introduction of offset printing, it became possible to operate presses at much higher speed than formerly obtainable with the relief process. This stimulated interest in methods of increasing the speed of relief presses. Substantial gains in speed have been made as a result of improved press design, improved papers, and in particular, improved inks, so that today sheet-fed relief presses run as fast as sheet-fed offset presses, and web relief presses run at even higher lineal speeds.

Printing involves the local application of ink to the paper in the form of dots, lines, characters, and solid areas. For certain purposes, the paper may be spot-varnished or overprinted, by which a special, oil-base varnish is applied to the paper. This is different from spirit varnishing, which is generally done with a lacquer applied over the printed paper in a separate operation. Spot-varnishing and overprinting produce a lower gloss than spirit varnishing. Spirit varnishes cannot be applied on a printing press because of their rapid drying properties which cause gumming of the transfer rolls.

Relief (Typographic or Letterpress) Process

The relief process is the most widely used of the printing processes. It is best suited for long runs to be printed in type and for jobs requiring fine detail in illustrations.

In the relief process, the ink is applied to a raised printing plate surface by a system of rollers made of rubber, glue-glycerine, vulcanized vegetable oils, or plastics. From the printing plate, the ink is then transferred to the paper under pressure. During printing, the ink film splits, part of the film transferring to the paper and part remaining on the plate. The ideal situation, from the standpoint of good printing, is to transfer as much ink as possible to the paper, because in this way the plate is cleaned for the next inking. If ink is allowed to build up on the plate, there will be a tendency to fill in the printing form.

Types of Printing Presses

Three types of printing presses are used for relief printing: the platen press, cylinder press, and the rotary press. The three types of presses differ mechanically, as shown in Figure XIX-1, but all are designed to accomplish the same purpose, namely, to bring the paper and the printing form together under pressure.

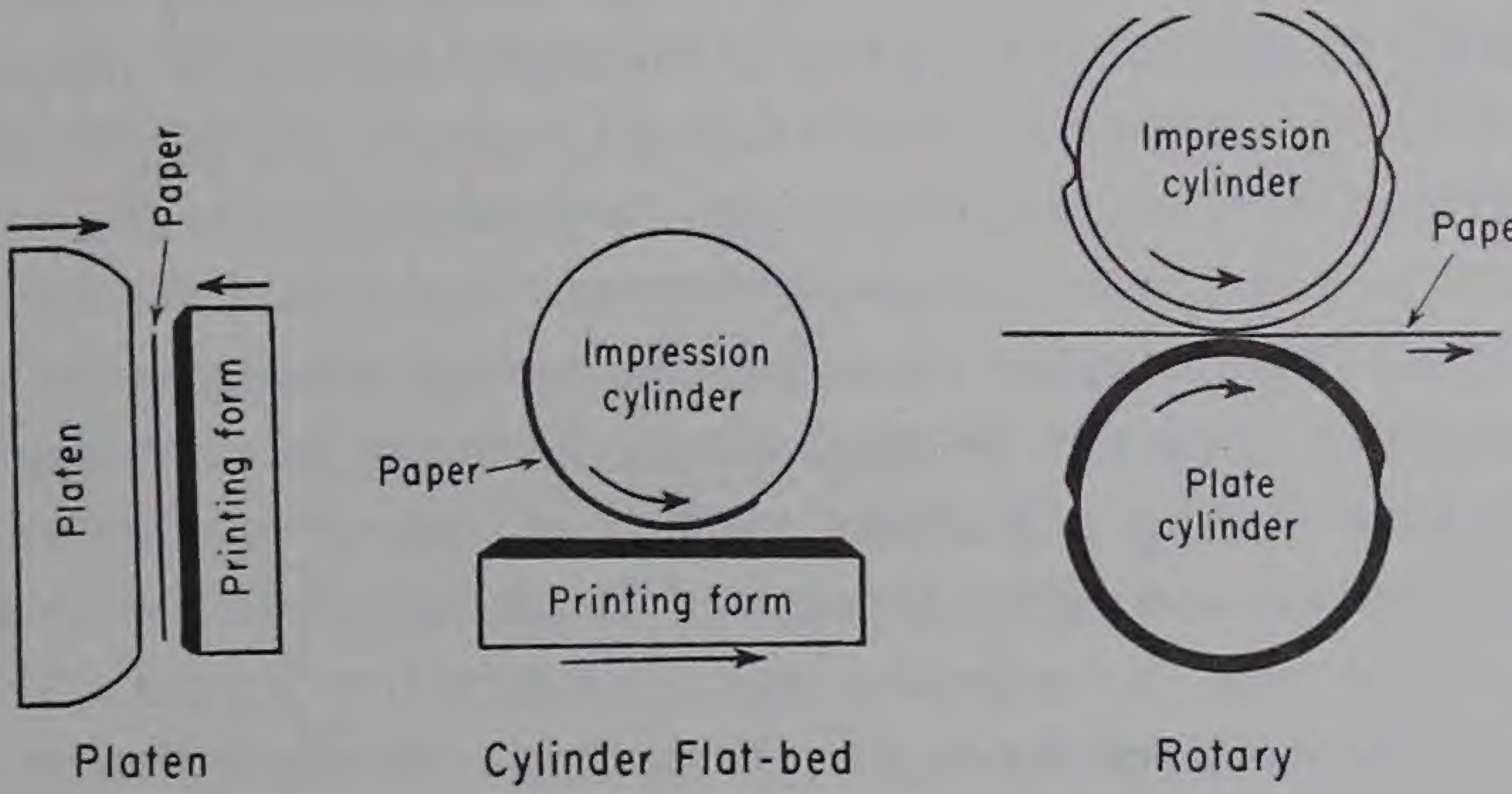

Fig. XIX-1. Types of presses for relief printing.

The platen press, sometimes called a job press, consists of two parts, the platen and the printing form. The printing form is inked by rollers and then a sheet of paper is forced against the form by means of a flat platen. The form and platen may advance toward each other, or the form may be stationary and the platen movable. All the form is printed at one time in a platen press. Platen presses are very useful for small forms but they do not provide as good impression as cylinder presses.

The cylinder flat-bed press consists of two parts, the impression cylinder and the printing form. The paper is fastened to the impression cylinder and moves with the cylinder. As the cylinder turns, the paper is brought into contact with the printing form which advances at the same rate as the cylinder is turning. When the impression is complete, the cylinder lifts and the printing form returns to its original position.

In the rotary press, the printing plates are fitted around a plate cylinder. The paper passes between the plate cylinder and the impression or backing cylinder, which rotate at the same speed. Rotary presses can be used for continuous web printing or for sheet fed printing. They are the most commonly used printing press. Web-fed rotary presses are much faster than sheet-fed presses.

Forms of Reproduction

Reproduction has three forms: type, line, and halftone. These are discussed below.

Type Reproduction. Type consists of letters, numbers, and characters. Type can be set as individual movable pieces by hand, or set mechanically in the form of slugs, or reproduced from typewritten copy. Type is set by hand only when small amounts of copy or special forms are involved. Hand setting involves the arranging of individual pieces of type in a composing stick, placing the set type in a form and locking in place. In production printing, intertypes and linotypes, which are power-driven machines operated by a keyboard, are used to cast slugs of type containing all the letters for each line in one piece, matrices being used for the casting of the slugs from molten metal. Another mechanical process is the monotype.

Typewritten copy can be photographed for use in photoengraving.

Photo-type setting is a direct method of setting type matter for lithography in which the photo-typesetter functions similarly to a linotype machine except that it composes type photographically.

Many different type faces are grouped into eleven different classifications, based on origin and general characteristics. The proper type face is determined by the type of printing process, finish on the paper, and by the artistic effects desired.

Line Reproduction. Line reproduction is concerned only with full color values, e.g., black, white, or colored, because line reproduction lays down the ink in the form of lines or solid areas with no shading in between. Until the invention of the halftone process, artists were employed to make line drawings for illustrations. Although this kind of work has been greatly reduced in recent years, line cuts are still used for the reproduction of pencil and ink drawings and for hand lettering.

In preparing a line reproduction or cut, a negative must first be made. There are two methods by which this may be done, the wet plate method and the dry plate method. In the wet plate method, this is done by (*1*) coating a piece of clean plate glass with albumen, (*2*) coating with collodion, (*3*) treating with silver nitrate, and (*4*) finally exposing in a camera to the drawing or photograph to be reproduced. The negative thus produced is stripped from the glass and reversed on another glass plate. This plate is used as a negative and placed with film side next to a sensitized zinc plate coated with albumen and bichromate of ammonia. The assembly is then exposed to strong arc light which hardens and insolubilizes the portions of the coated plate corresponding to the light areas on the negative. The plate is covered with ink and washed in water to remove the unhardened portion of the coating. Next, the plate is treated with dragon's blood (resin) to protect further the hardened areas, and the plate is placed in dilute nitric acid to etch the unexposed areas of the plate. Treatment with dragon's blood and etching is repeated until the correct depth of cut is obtained, after which the plate is touched up and cleaned. The printing areas of the plate consist of a series of solid lines or solid areas which are broken up by non-printing recessed areas which do not receive ink in the printing operation.

Halftone Reproduction. Shadings can be obtained with the halftone process ranging all the way from solid colors to whites. The halftone process is used in relief and planographic printing for pictorial reproduction.

A relief halftone plate consists of a mass of raised areas or dots which prints ink to form a corresponding mass of dots on the printed paper. The size of the dots on the printed paper determines the gradation in tone of the picture. The larger the dots and the closer they are on the paper, the deeper the color of the impression. The smaller the dots, the farther apart they are, the lighter the color. When a black ink is used, it is possible to obtain color ranging from black through gray to white, depending upon the size of the dots.

The copy for halftone reproduction is in continuous tone which may be in the form of a photograph, artist's painting, and copy which requires the middle tones or halftones. If colored copy is reproduced in black and white, the colors reproduce in a range from almost white to black. The original blue reproduces almost white, white reproduces a light gray, gray reproduces a light gray, green reproduces a dark grey, and brown and red reproduce almost black.

A halftone plate is made from the copy by first photographing the copy through a special screen to produce a halftone screen negative. The screen consists of two sheets of glass ruled with parallel lines which are cemented together with the lines on one plate at right angles to the lines on the other plate to form a screen. The distance between the lines on the screen determines the number of dots on the plate. The size of the dots depends upon the detail in the copy. The highlights of the copy reproduce as small dots, widely spaced, whereas the dark areas reproduce as larger dots, closely spaced. The number of dots is the same in both the highlights and the dark areas since the same screen size is used.

The sensitized plate used for preparing relief halftones is either a copper plate sensitized with a mixture of photoengraver's glue (fish glue) and ammonium bichromate, or a zinc plate sensitized with albumen and ammonium bichromate or shellac and ammonium bichromate (cold top enamel). The plate is prepared by making a contact print of the screen negative onto the sensitized surface, after which the plate is washed in water to remove the soluble portion of the coating. The light-hardened portion on the plate is left intact, and this is further hardened by heating. The unprotected areas of the plate are then removed by etching (in ferric chloride) or by electrolysis. The plate may then be touched up, i.e., etched deeper to brighten the printing, or burnished, if a deeper color is desired. Depth of etching varies from about 0.002 to 0.003 in. for the highlights to about 0.001 to 0.002 in. for the shadows.

Most commercial work is done with screens ranging from 50 to 133 lines per inch. Screens from 50 to 100 lines are considered as coarse, while screens from 110 to 200 lines are considered as fine. A 133-line screen produces in the neighborhood of 17,000 dots per square inch. Each dot must stand apart on the printing plate to receive printing ink, and each dot must be faithfully reproduced on the paper. If more than 25% of the dots are missing or distorted, the printing will be worthless.[1] Fine workmanship in the preparation of the plate and smooth-finished paper are required to obtain satisfactory results from fine screens (see Table I).

Multicolor Printing. The wide range of colors usually found in colored copy can be faithfully reproduced by multicolor printing, but the effects are usually obtained by printing only three or four colors. The basic colors used are red, yellow, and blue. These colors are enough to produce any desired shade, but for best results a fourth color, black, is used.

The copy for color printing can be a water color drawing, an oil painting, a transparency, or other work. If the copy is art work, separate negatives are prepared for each color by photographing through color filters to eliminate all colors from the negative except the color wanted. If color correcting is necessary, this can be accomplished by working directly on the halftone dots or by changing the stained masks used for holding back the colors.

In preparing screen patterns, screen angle rotation is used in making the plate. The usual screen angle for the separation of color copy is 30°. In printing four colors, the three strong colors (e.g., red, blue, and black)

[1] Talk by Mr. R. A. Diehm, reprinted in *Tappi 33,* No. 2: 42A, 44A, 46A, 48A (Feb., 1950)

may be separated equally at 30° and the fourth color (e.g., yellow) positioned between the red and blue at 15°, i.e., yellow at 90°, red at 75°, blue at 105°, and black at 45°.[2]

Separate plates must be prepared for each color and each color printed separately. Transparent inks are used so that the desired colors are reproduced by the overlapping dots of ink on the paper. The classical method is to print the yellow plate first, then the red plate, then the blue, and lastly, the black plate. Sometimes, however, the black is placed down first as a key plate for registration. Some pressmen put the red down first and others the blue, depending upon the color effect that they want.

Printing Plates

As mentioned earlier, relief printing is done from raised surfaces which may be metal, wood, rubber, linoleum, or other suitable material. The earliest typographic printing, practiced by the Chinese as early as 1000 B.C., was done from wood blocks on which the characters were carved in reverse by hand. Wood-block printing was used extensively in Europe and continued in use there until movable type was invented about 1450. The invention of movable type was a notable advance in printing, since it permitted the reuse of individual pieces of type for many jobs. Hand setting of movable type is still used for small jobs, display type, and special forms, but for production jobs, movable type has been discarded in favor of individual solid plates because of the very high machine speeds used on modern presses and the necessity of running the same job on several presses at the same time.

Electrotypes and Stereotypes. The original type or halftone plate may be used for printing short runs of less than 50,000 impressions, but for longer runs, duplicate plates must be made from the original forms. Duplicate plates are made as spares in case of abnormal wear of a form, or in the case of batter or damage to the first plate. They are made when more than one up is to be printed, that is, when the same order is printed on more than one press at a time, and when two or more copies of the same form are printed on a single large sheet and separated later. There are two principal methods of making duplicate plates, electrotyping and stereotyping.

Electrotype plates are used when it is desirable to reproduce a number of plates from the original type or halftone plate as, for example, when long-run, high-grade printing jobs are required for rotary printing of flat sheets. Electrotypes can be made by pressing the original plate into wax and coating the depressed wax surface with graphite to make it conductive, but a more modern technique is to mold in tenaplate and vinylite, and spray with silver salts to give the electric contact for plating. The matrix is then electroplated to deposit a layer of copper about 0.006 to 0.008 in. thick. The resulting copper shell is then removed from the wax and filled with electrotype backing material, a special alloy similar to type metal. After the plate has been filled, the back is planed to a definite thickness, the non-printing areas are routed out, and the plate is mounted on wood, metal, or patent steel base and fitted to the press. Electrotype plates give an average run of 1,000,000 impressions. If there are prospects of abnormal wear due to the type of paper or ink used, they can be run in nickel or chromium plating.

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[2] D. J. Andella, *Paper Trade J. 128,* No. 4: 35–39 (Jan. 27, 1949)

Stereotype plates are widely used for the printing of newspapers and advertisements, and to some extent for the printing of magazines when screens of 85 lines or less are used. In making a stereotype from the original plate, a mold of the plate is made in matrix paper (flong) by pressing the slightly moistened matrix paper upon the plate under high pressure. The matrix paper is a heavy, absorbent paper that has a high stretch and compressibility and a smooth surface so that it will accurately reproduce the detail in the plate surface. After molding, the paper is dried and placed in a molding box which is filled with molten stereotype metal consisting of a mixture of lead, tin, and antimony. This forms the stereotype plate. This is a rapid and relatively cheap method of reproducing plates.

Special Printing Plates. Because of the non-flexible nature of the metal plates used in relief printing, only those papers having a high resiliency and a reasonably smooth surface can be printed when fine details are desired. This limitation on papers suitable for relief printing has stimulated interest in the use of flexible plates which would permit the printing of rough papers. Rubber plates made from plastic molds have been used for the printing of rough-surfaced papers for paper bags and sales books. These plates are good for about 200,000 to 500,000 impressions when oil-base inks are used. A special combination machine known as a printer-slotter equipped with rubber printing plates is used for printing corrugated boxes. Rubber plates are also used on aniline printing presses and these are good up to 1,000,000 impressions. Plastic plates molded from the original metal plates have been used to a limited extent for specialized printing.

Makeready

The basis of good printing by the relief process is a firm impression. After the plate is prepared, it must be properly planed down and adjusted on the press to secure the desired impression on the paper. However, these steps by themselves are not enough to insure a uniform impression because of lack of uniformity in the printing form, and consequently the pressman must further adjust the impression by the process of makeready.

Makeready involves the building up of a layer of packing of the proper thickness upon the impression surface on which the paper is to be printed. This involves the building up of a number of plies of paper under the tympan, the top manila sheet (usually oiled) to which the guides are fastened and on which paper is printed. On a rotary press, this involves the building up of a packing of a number of sheets around the impression cylinder under the top sheet. After this initial preparation, a sheet of paper is fed through the press and printed. This sheet, which is called the "makeready sheet," reveals the inequalities of impression and indicates the amount of correction necessary in the packing. Corrections are made by applying makeready tissue to the makeready sheet to increase pressure where the impression is weak and then substituting this spotted up sheet for one of the sheets used in the packing. A second sheet of paper is then printed, and if the impression is still not satisfactory, a second makeready sheet is spotted up with makeready tissue and placed on the cylinder under the top sheet. This is continued until the desired impression is obtained. The final packing should be firm and solid, since a soft, spongy packing will result in embossing of the printed paper toward the end of the press run.

An absolutely flat makeready is not always desirable, since extra impression may be required in certain areas of the printing. Solid printing areas and heavy, large type require extra impression, and consequently an extra thickness of tissue is applied on the makeready sheet where these appear. In the printing of halftone plates, an overlay is used to vary the thickness of the makeready so that the greatest impression is obtained in the solid areas and the least impression is obtained in the highlight areas. Generally, from 0.001 to 0.003 in. more of printing pressure is required in the solid areas of a halftone compared to the highlights of the halftone.

Relief Printing Inks

Printing inks consist of a pigment suspended in a liquid medium called the vehicle. The early relief (letterpress) inks were made by the printer who boiled linseed oil until it had the desired consistency and then mixed this oil with carbon black. Today, the printer can buy printing inks which vary from thin fluids to viscous or plastic materials. There are many types of printing inks.

Pigments are used in printing inks to impart color, opacity, body, and proper flow to the ink. In most cases, black inks are used against a white paper background, since this furnishes the maximum contrast, but black inks are also widely printed on colored papers. The hiding power of the pigment is due to the interception of light rays, by absorption, reflection, and refraction. The results obtained depend upon the type of the pigment, the nature of the pigment surface, and the amount of pigment surface exposed. Hiding power increases as the pigment is subdivided until the dimensions approach the wavelength of light. With further subdivision, hiding power decreases.

Carbon black and lampblack are the two principal pigments used in black inks. Carbon black enjoys a far greater usage than lampblack because it dries to a higher finish and has a greater tinctorial value. Carbon black particles are nearly spherical in shape, are quite uniform in size, and have a large surface area, because of their internal porosity.[3]

Many inks contain colored pigments. Natural pigments which have been treated so that they are free of grit are sometimes used in printing inks, e.g., umber, ochre, sienna, Indian red, and iron yellow. However, most of the colored pigments are synthetic organic and inorganic pigments, some of which include the iron blues, chrome yellows, chrome greens, vermillion (mercury sulfide), cadmium red, cadmium yellow, zinc yellow, calcium, barium, or aluminum lakes of acid dyes, insoluble azo dyes, phosmolybdic or phosphotungstic lakes of basic dyes, and white pigments (titanium dioxide, lithopone, zinc white and white lead).

Metallic pigments (e.g., aluminum, copper, or brass powders) are used in special inks for the printing of booklets, advertisements, and labels. The important consideration in inks of this type is a high leafing value, since this increases the brilliance of the film. The size, shape, and surface conditions of the pigment flakes are factors in determining the leafing qualities. Aluminum pigment is generally coated during manufacture with stearic acid which forms a thin, oriented film on the surface of the aluminum and causes the flakes to stay on the surface of the vehicle. Aluminum powders are fairly stable, but bronze inks should be used as soon after preparation as possible and agitation of the ink held to a minimum, since bronze pigments tend to react with the fatty acids in the vehicle and become dull. In printing with metallic inks, heavy ink films should be applied under a minimum of pressure in order to obtain maximum leafing.

Extenders or fillers are sometimes added to printing inks to reduce the price, extend the coverage, and increase the body of the ink. Some of the common extenders are barytes, clay, blanc fixe, whiting, and silica. Other fillers and loaders may be added, but they should be used with caution, since too much extender results in an ink which lacks snap.

Increasing the pigmentation of the ink increases the color value and improves the print quality. However, in practice, pigmentation is limited by the working properties of the ink on the press and the absorbency of the paper being printed. Too little pigmentation results in a long ink, whereas too much pigment results in a short ink.

The compounding of printing ink requires careful control by an expert ink maker. The vehicle is first added to a large mixer and then the pigments are added gradually with stirring, after which the mixture is ground in a roller or ball mill until the pigment agglomerates are dispersed to the correct particle size. Milling affects the viscosity, interfacial tension, and degree of dispersion of the ink. Inks which have been poorly milled will give trouble by filling in of the plate. The vehicle in poorly milled ink tends to separate from the pigment and penetrate excessively into the paper, and for this reason, an ink which tends to penetrate the paper excessively can sometimes be improved by a second milling. Ink which is well dispersed immediately after milling, but tends to flocculate later, may cause a filling-in of fine halftones, but such an ink can usually be redispersed by relatively weak mechanical forces.

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[3] O. J. Brown and W. R. Smith, *Ind. Eng. Chem. 34*, No. 3: 352–355 (Mar., 1942)

Printing Ink Transfer. It is desirable to say something about the mode of transfer of ink from the ink rollers to the printing plate and from the printing plate to the paper. The amount of ink applied to the plate by the rollers is controlled by setting the fountain keys which open or close the fountain and then adjusting the stroke of the ink roll to increase or decrease the ink flow. The proper adjustment of the fountain is very important, best results being obtained with the minimum amount of ink necessary for the desired intensity of color. Proper fountain adjustment, together with proper preparation of the plate and makeready, govern the relative amount of ink deposited in the various printing areas on the paper. These variables are controlled so that the areas of solid printing and areas of heavy type receive the greatest amount of ink. When halftone plates have solid areas which contain halftone dots, the pressman may force the plate to fill up the spaces between the dots so that this area prints solid.

When printing on a non-porous surface (e.g., metal or cellophane), the ink film tends to split fifty-fifty between the printing plate and the surface being printed. In the printing of a porous material such as paper, more than 50% of the ink is transferred, the exact amount depending upon the porosity and smoothness of the paper and the printing pressure. On very porous papers, the ink readily penetrates the paper, resulting in easy removal of ink from the plate. Inks are transferred to paper by a combination of absorption and adhesive strength. The greater the effect of the adhesive strength and the less the effect of absorption, the brighter the printing.

The thickness of the ink film on the printed paper has an important effect on the quality of the printing. Thick films improve the contrast, whereas thin films give a gray appearance to the print. However, excessively thick films may result in messy printing. In the case of newsprint, Prior[4] found that a film of 0.45 micron was too light, a film of 1.1 microns about normal, and a film of 1.8 microns too thick. For art printing, he found 1.9 microns about right. Since ordinary paper is about 100 microns in thickness, it can be seen that the film of ink is relatively thin in comparison with the paper. Prior has shown that most ink films have a reticulated appearance under the microscope, caused by alternate thick and thin areas of ink. He attributes this unevenness to a pulling out of the ink into fine threads, which cause it to print on the paper in the form of little heaps. The ink receptivity of the paper, as well as the flow properties of the ink affect the evenness of ink coverage.

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[4] P. H. Prior, *Paper Trade J. 111,* No. 15: 223–228 (Oct. 11, 1935)

Drying Oil-Base Relief Inks. Inks containing a drying oil base (e.g., linseed oil) have been the standard inks for ordinary relief printing for many years. The functions of the drying oil in an oil-base ink are to impart the necessary fluidity to the ink and to act as the binding and hardening agent when the ink film dries on the paper. (Drying oils are considered to be those oils with an iodine number greater than 120.) Vegetable oils (linseed, china wood or tung, and perilla) are most commonly used in this type of ink. Linseed oil produces a fairly soft, slow-drying film, whereas china wood oil is very rapid drying. All oils must be heated or bodied to develop the correct viscosity before being mixed with the pigment prior to ink manufacture. This bodying of the oil changes the molecular arrangement and increases the drying rate. Bodied oils are sold as varnishes or stand oils ranging from No. 00000 (the lightest) to No. 9 (the heaviest).

During drying of the ink on the paper, the ink is transformed from a fluid or semi-fluid state to a solid state. Drying takes place in two ways, by absorption of ink vehicle into the pores of the paper through capillary action and by a hardening of the ink film on the paper. The first is governed by the viscosity of the ink and the porosity of the paper and takes place very rapidly. The second, or hardening, stage involves a polymerization and oxidation of the oil vehicle, both of which take place very slowly. During this stage, the drying oil absorbs oxygen from the air, thereby changing from a viscous liquid to a hard, solid film which binds the pigment particles tightly to the paper.

If the ink dries too fast, the ink becomes tacky on the rollers, resulting in picking, whereas if the ink dries too slowly, the print smears on the paper and the ink feels wet. In order to control the rate of drying of drying oil-base inks (and some non-drying oil-base inks), it is necessary for the printer to add driers to the ink. Driers are organic salts (e.g., the resinates, linoleates, octoates, and naphthenates of zinc, lead, cobalt, or manganese) which increase the rate of drying of the ink film on the paper by increasing the rate of absorption of oxygen. Cobalt makes the most potent drier, being four to five times as effective as lead and manganese. In general, cobalt is classed as a surface drier, lead as an internal drier, and manganese as a combination surface and internal drier. Driers sometimes lose their effect after the ink has been standing around for some time. The loss is greater for inks pigmented with lake colors containing aluminum hydrate and for carbon black, and for this reason, a relatively high percentage of drier is used in inks containing these pigments. The loss in effectiveness of driers in the presence of these pigments can be explained by the fact that the active metal group of the drier becomes adsorbed next to the pigment, leaving the inactive organic group projecting into the vehicle.[5] Certain pigments can adsorb large quantities of drier, although recently improved driers have been developed to overcome this difficulty.[6] Too much drier is detrimental to the working properties of the ink, and in some cases may actually retard the drying. Generally speaking, more drier is required during the summer months when the humidity is high and drying is likely to be slower. Inks to be overprinted are sometimes made slow-drying on purpose in order to prevent them from hardening before the succeeding colors are printed over them. Anti-skinning agents, which are in reality antioxidants, may be added to prevent the formation of a skin on the ink, and while these agents offset the effect of the drier to some extent, they are useful in preventing drying or hardening of the ink on the press.

Natural and synthetic resins are frequently used in printing inks, either in combination with drying oils or alone as the only vehicle in special solvent type inks. Resin-oil combinations, known as oleoresinous varnishes, are made by mixing the resin with the drying oil (linseed or tung) and heating until the desired viscosity is reached. A very fast-drying varnish can be made by heating rosin-modified phenolic resins with china wood oil at 450 to 580° F. for thirty to thirty-five minutes. Oleoresinous varnishes containing drying-oil alkyds of the short-oil type, or rosin-modified maleic type resins can be made in approximately the same way. Oleoresinous varnishes have, in general, higher gloss and better holdout properties than regular linseed oil varnishes, and for this reason, are frequently used in making high-gloss inks. The presence of the resin improves the sharpness of detail by keeping the ink on the surface of the paper, gives the ink non-scratch properties by increasing the hardness, and improves the adhesion, which is a particularly important factor in the printing of non-porous materials such as cellophane and wax paper. Oleoresinous varnishes ordinarily have improved resistance to alkali, acid, and greases; for example, a resin-modified drying oil containing a coumarone-indene resin is said to make an alkali-resistant ink suitable for printing soap wrappers.[7] Because of the greater grease and chemical resistance, the higher gloss, and the improved holdout properties, compared with ordinary varnishes, clear oleoresinous varnishes are widely used for overprinting. Where special raised effects are desired, e.g., in the printing of letterheads, business cards, and announcements, the ink may be dusted with a resin which adheres to the wet ink film and is fused there upon baking. The effects resemble those obtained in engraving.

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[5] W. F. Harrison, *Ind. Eng. Chem. 25,* No. 4: 378–381 (Apr., 1933)

[6] W. C. Walker, *Tech. Assoc. Papers 31:* 440; 442 (June, 1948)

[7] I. Bernstein, U. S. 2,401,898 (June 11, 1946)

Waxy or greasy compounds, e.g., petrolatum, paraffin, and wool grease, are sometimes added to printing ink by the printer to reduce the tack and prevent offset. Waxy or oily substances should not be used if overprints are to be made, since they tend to migrate to the surface of the ink film during drying, making it difficult for other colors to trap over them because of a lowering of the tack of the ink.

The rheological (flow) properties of the ink determine its working properties on the press and its penetrating qualities on the paper. Voet and Brand[8] found that the rate of penetration of printing ink into paper is directly proportional to the fluidity of the ink vehicle, but not to the fluidity of the compounded ink. The temperature of the ink is important to the extent that it affects the fluidity of the ink vehicle. Printing inks are non-Newtonian fluids generally exhibiting plastic, pseudoplastic, dilatant, or thixotropic properties. Inks are, however, subject to high rates of shear on the printing press. This tends to overcome any yield value and thixotropy, thus permitting even distribution of ink on the rollers.

For best results, printing ink should have the highest viscosity and yield value consistent with good operation on the press and good printing properties on the paper being used.[9] High yield value alone results in an ink which is too short; the ink tends to back away from the fountain. Backing away from the fountain caused by too short an ink can be corrected by adding a bodied varnish, e.g., No. 2, No. 3, or No. 4. Too short an ink results in mottle, a condition of ridges in the ink film. Papers of medium absorbency can be printed with inks of high viscosity and high yield point, but the flow properties of the ink must be such that the ink distributes well on the press. For relatively non-absorbent papers, the ink maker may add a penetrant, although usually a fairly heavy bodied varnish with considerable tack will produce good results. When printing non-absorbent paper, a small amount of light mineral oil may be helpful in reducing the viscosity of the ink, thereby producing more rapid penetration into the paper and reducing offset. Thinner inks are required the faster the speed of the press.

A subject closely related to flow is the tack of the ink, which is commonly visualized as the pull resistance exerted by the ink on the paper surface. The pull exerted between the printing plate and the paper depends upon the type of ink, rate of separation of the plate and paper surfaces, area of contact, and film thickness. At the high rates of shear existing on a press, plastic viscosity is the dominant rheological factor affecting tack, yield point being of little influence. According to Voet and Geffken,[10] the dominant factor in ink tack is not the force, but the energy of film separation which they found to be proportional to the plastic viscosity of the ink raised to the 1.5 power. They visualize film separation as taking place primarily by rupture in a solid pattern resulting from transversal vibrations induced at the paper-ink interface. A certain amount of tack is necessary to cause adherence of the ink to the paper; if the tack of the ink is not sufficient for the type of paper and press conditions used, the reproduction will be poor. On the other hand, too tacky an ink is likely to rupture or pick the paper surface. In multicolor printing, the various inks must be graded in tack to secure proper trapping, i.e., blending of the different colors on the paper. The first-down ink (usually yellow) must be relatively tacky so that it will lift the second-down ink (usually red). The second-down ink should be more tacky than the third-down ink (usually blue), which in turn should be more tacky than the last-down ink (usually black). Inks differ in their rate of increase of tack with increased press speed,[11] and hence it is possible for two inks to change their relative order of trapping as the speed of the press is increased, with the result that false color values are produced. The tack of ink can be measured by special tackometers.[11] The tack can be measured qualitatively by an experienced pressman by rubbing a small amount of the ink into a thin film on a piece of paper or a glass, and then repeatedly pressing a finger on the film and pulling it away to measure the pull resistance developed by the ink.

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[8] A. Voet and J. S. Brand, *Paper Trade J. 122*, No. 24: 264–269 (June 13, 1946)

[9] H. J. Wolff, *Paper Trade J. 116*, No. 12: 132–134 (Mar. 25, 1943)

Solvent Heat-Set Relief Inks. The trend in printing is toward higher press speeds, and since the limiting factor in operating at higher speeds is the drying of the ink, many new rapid-drying inks have been developed. One of these new inks is a solvent-base, heat-set ink. Solvent type inks have been used for many years in the gravure process. Relief inks having improved drying properties were first made by adding a volatile solvent to regular relief inks, but within recent years, improved solvent heat-set inks have been developed for relief printing. These inks have made possible greatly increased printing speeds on rotary web presses.[12]

Heat-set inks (Flash-Dri, Heatset, or Vaporin) for relief printing contain a high percentage of volatile solvent having a definite evaporation temperature. The solvent must be relatively non-volatile at room temperature and very volatile at elevated temperatures, or it may be a mixture of sol-

[10] A. Voet and C. F. Geffken, Paper given at 35th Annual Meeting of TAPPI, Commodore Hotel, New York City (Feb. 23, 1950)

[11] H. Green. *Industrial Rheology and Rheological Structures*, p. 133, John Wiley & Sons, New York, N. Y. (1949)

[12] R. L. Drake, *Paper Mill 63*, No. 29: 24–26 (July 20, 1940)

vents of different volatilities. Resins are used as the binder. A typical composition of a heat-set ink is as follows: pigment, 20%; resins, plasticizers, waxes, 45%; solvent, 35%. Recently four-color process inks in heat-set formulation have been developed.

After printing with a heat-set ink, the paper is passed through an oven where a gas flame plays upon the printed surface, igniting and burning the volatile constituents of the ink and baking the resinous binder. Other methods of drying employ hot air chambers, infrared units, or steam-heated drums which vaporize the solvent, leaving the resin to bind the pigment particles. The heated paper is then passed over cooling rolls to bring the paper back to room temperature and to complete the setting by making the ink tack-free. Separate drying units are generally used for each side.

Heat-set inks are used mostly for the relief printing of magazines and catalogues where instant drying is desired. (Special types have also been developed for planographic printing.[13]) The chief disadvantage of heat-set inks is the necessity of subjecting the paper to high temperature, which sometimes causes shrinkage, excessive static electricity, and a dehydration of the paper. The strength of the paper is often reduced by as much as 20% during drying, which must be offset by the use of more expensive papers. The heat-set process is ordinarily limited to web presses.

Cold-Set Relief Inks. Cold-set ink is another attempted development to speed up the drying process. So far, cold-set inks are not very successful and have not been used to any appreciable extent. This type of ink is based upon the use of a thermoplastic resin which is solid at temperatures below 140 to 180° F., but which becomes fluid when heated to temperatures above 200 to 220° F.

Cold-set inks are picked up from heated fountains by means of heated rolls and applied to hot printing plates from which they are printed on the paper. The fountain, ink rolls, and printing plate must all be heated to a temperature above the flow point of the ink (approximately 220° F.). When the hot ink contacts the relatively cool paper surface, the layer in contact with the paper increases in viscosity while the layer next to the heated printing surface remains highly fluid. Since the viscosity of the ink is greatest in the layer closest to the paper surface, the normal relationships in printing ink transfer are not present, and the film tends to break near the printing plate, leaving very little ink on the plate.[14] Because of this, there is less tendency toward picking. For the same reason, cold-set inks do not penetrate to any extent, but tend to remain on the surface of the paper in sharp relief. Penetration, if desired, can be obtained by passing the printed paper over a heated cylinder to soften the film and permit

[13] *Am. Ink Maker*, pp. 21–24 (Dec., 1944)

[14] F. G. Breyer, *Paper Trade J. 110*, No. 24: 315–316 (June 13, 1940)

further penetration. The final film is not very hard, and the major problem has been in finding an ink which is tough enough to withstand scuffing.

Vapor-Set Relief Inks. Vapor-set inks (Vaposet, Moisture-Set, Hydri, etc.) are inks based on a different principle from other inks in that the ink does not harden by oxidation or by evaporation, but rather is changed from the liquid to the plastic state by coagulation of the ink through the absorption of moisture by the ink film. The ink contains a vehicle composed of a synthetic resin and an organic solvent (alcohol) having a high boiling point and a low vapor pressure.[15] The resin is soluble in the organic solvent and a limited quantity of water, but is insoluble in the presence of a higher percentage of water. One patented type of vapor- or steam-set ink is based upon the use of a special, hard, high-melting rosin-modified maleic resin which is dissolved in diethylene glycol. A suitable formula[16] for the vehicle is: rosin-modified maleic resin, 100 parts; diethylene glycol, 100 parts. Add resin to diethylene glycol and heat to 300° F. and hold for ten minutes until a clear solution is obtained. The water tolerance of the above vehicle is 3.0 to 3.5 cc. per cubic centimeter of vehicle. When the water content of the ink exceeds this critical value, the resin is coagulated and the pigment is occluded and precipitated with the vehicle in the form of a hard film.

Under ordinary pressroom humidities, the ink maintains its fluidity, but when the printed paper is subjected to a condition of high moisture (e.g., when the printed paper is sprayed with steam or water vapor), the ink film picks up moisture and forms a thin, hard layer on the surface. The exterior of the ink film is dry and hard, which prevents the printed sheet from offsetting, but underneath the surface the ink remains in a permanently plastic condition. Even when not sprayed, this ink will usually set and harden on most papers in ten to thirty minutes.

The advantages of this type of ink are greater speed in printing, elimination of offset, lack of any odor from oxidation of vehicle, and freedom from bleeding upon waxing. These inks are particularly suitable for printing waxing papers (bread wrapper), chewing gum wrapper, multiwall kraft bags, and paper carton stock to be used for the packaging of foodstuffs. On kraft bags, the high moisture content of the paper facilitates rapid setting even without the external application of moisture.[17] Some of the earlier steam-set inks were unstable under high moisture conditions, but recent changes have improved the stability.[18, 19] These inks cannot be used in planographic printing because of the presence of water.

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[15] D. R. Erickson and F. D. Elliot, *Paper Trade J. 112,* No. 22: 273–274 (May 29, 1941)

[16] Tech. Bulletin, "Amberol," pp. 14–15. Rohm and Haas Co., The Resinous Products Division, Philadelphia, Pennsylvania (Apr., 1948)

[17] Report on talk given by J. Watson, *Tappi 33,* No. 6: 60A, 62A, 64A (June, 1950)

General Requirements of Papers for Relief Printing

Each printing process has definite requirements which a satisfactory paper for that process must meet. In the following sections, the important properties of papers for relief printing are discussed. Many of these properties are important for other printing processes as well, and in many cases may be considered as general requirements for all printing papers.

Among the grades of paper used for relief printing are book papers (coated and uncoated), catalogue, news, mimeograph, folding boxboard, bond, ledger, cover, blotter and bristol. The majority of book paper is made from a furnish of bleached soda or deinked stock, plus some sulfite or sulfate stock. A typical furnish would include 20 to 30% sulfite, and 70 to 80% soda or deinked stock. Groundwood pulp is used in some grades mainly to lower the cost and also to increase the opacity, to reduce strike through, and to improve the uniformity of printing. Rag or high-quality chemical pulp may be added if the printed paper must stand considerable handling or folding in use or if permanence is required. The stock for book paper is generally beaten very lightly. The sizing is light or eliminated entirely, since the printed paper is generally not written upon with aqueous inks. Up to 30% filler may be added.

Printability and Print Quality. Printing may, for convenience, be divided into two major steps, (*1*) transfer of ink to the paper and (*2*) drying of the ink film on the surface of the paper. The transfer of ink is influenced by the ink receptivity and smoothness of the paper, whereas the drying of the ink is influenced by the oil absorbency of the paper (when oil-base inks are used) and the drying characteristics of the ink. It should be emphasized that both the transfer of the ink and the drying of the ink are functions of the paper, as well as of the ink.

The printer commonly speaks of the printability of paper. Printability is not an accurately defined property, but instead is a broad, general term referring to the property of a paper which yields printed matter of good quality. The best method of testing paper for printability is by printing runs on a commercial printing press. The next best method is by laboratory tests on a proofpress. An engraver's proofpress such as a No. 4 Vandercook or Hacker press[20] is suitable, but several alterations in the

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[18] F. J. Jeuck and C. A. Rietz, U. S. 2,390,102 (Dec. 4, 1945)

[19] *Am. Ink Maker 25,* No. 4: 42–44 (Apr., 1947)

[20] Proofpresses are made by Vandercook and Sons, Chicago, Illinois, and Miehle Printing Press and Mfg. Co., 2021 Hastings, Chicago, Illinois

press are desirable for best results.[21] Glue-coated rollers are recommended for use with heat-set inks, whereas synthetic rubber rollers are necessary for use with moisture-setting inks. Means of applying an ink film of uniform thickness to the plates must be used; the ink should be applied by volume, rather than by weight, since inks differ in specific gravity. Accurate plate height is essential and a micrometer should be used to check the plate height and packing. The impression cylinder of the press is undercut a definite amount and then built up with a patent base to provide the desired printing pressure.

Considerable skill and judgment is required in the testing and grading of papers on a proofpress. However, when the test is properly carried out under strict control by a skilled operator, it is possible to obtain considerable information relative to the printing qualities of the paper. An indication[22] of the printability of the paper can be obtained by comparing the print obtained on the unknown sample with the print obtained on a standard paper for evenness of coverage, mottling of solid colors, and sharpness of detail in halftones. A value indicative of the ink receptivity can be obtained by measuring the amount of ink left on the printing plate. The ink absorption of the paper is indicated by the evenness of absorption of ink by the paper. Any tendency toward offset can be detected by laying a sheet of paper over a freshly printed specimen and feeding the two papers through the press. The picking tendency of the paper can be measured by successively printing the specimen with inks of progressively increasing tack.

If a commercial press or a proofpress is not available for testing the printability of paper, simpler methods can be used. In one method of testing, originated by Bekk and used by others,[23-25] a weighed amount of printing ink is transferred to a piece of plate glass of known area. The ink is spread over the glass in a film of uniform thickness, using a rubber roll. Two samples of paper, the specimen to be evaluated and a standard sample, are placed side by side on the inked glass plate, covered with several sheets of paper, and then a 25-lb. brass roller is rolled back and forth four or five times over the entire area. The samples are then removed from the plate and compared visually or photometrically for degree and uniformity of blackness. Printing smoothness and formation can be evaluated from the uniformity of the inked surface; ink absorbency can be evaluated from the blackness of the print.[26] This test is much simpler than testing on a proofpress and can be carried out quite readily by non-technical help. One significant difference between this test and the results obtained in commercial printing is that the paper is left in contact with the ink for a longer period of time, and only solid areas are printed.

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[21] O. P. Berberich, L. F. Engelhart and M. Zucker, *Paper Trade J. 127,* No. 7: 348–352 (Aug. 12, 1948)

[22] *Idem.*

[23] J. H. Bardsley and L. J. Morin, *Paper Ind. 29,* No. 3: 438–440 (June, 1947)

[24] G. E. Carlsson, *Pulp Paper Mag. Canada 40,* No. 7: 421–427; No. 8: 476–483 (June, July, 1939)

[25] J. H. Bardsley and L. Morin, *Pulp Paper Mag. Canada 48,* No. 3: 159–162, Convention Issue (1947)

The print quality of the final printed paper is determined by the printability of the paper and the method of operating the press. Among the elements determining the quality of the printing are the amount of contrast between the printed and unprinted areas, finish of the printed and unprinted areas, the uniformity of solid and halftone areas, legibility of printing, and show through. Print quality is usually measured by a visual examination of the print, but methods for measuring objectively the tone reproduction of halftone prints and the uniformity of solid prints have been suggested.[27]

Tone reproduction, or the faithfulness of reproduction of the printing plate, is highly important in determining the quality of halftone printing. Halftone dots produced by relief printing show a halo or doughnut effect caused by a ring of ink of greater thickness around the circumference of the dot. This may be due to too much ink or to the inking rollers pressing against the top of the dots, leaving a thin film in the center and an overhanging rim of ink around the edges. Because of the pressure used in relief printing, there is generally some embossing on the back of the printed paper. This is different from the effect obtained in offset printing where the halftone dots produced are solid black without squeeze and show no embossing on the back.

In solid prints, uniformity or evenness of color density and glossiness of the ink film are the important factors in determining print quality. Solid prints sometimes show mottle or bright spots which lower the print quality. The thickness of the ink film and degree of blackness or density of the ink are important factors.

Ease of reading is determined in large part by the contrast between the ink and the paper surface. Black ink on white paper gives the greatest contrast because white paper reflects the greatest amount of light and black ink reflects the least amount. Brightness is the most important factor, but the contrast is not only one of brightness, but also one of hue and saturation. Printing on off-color or tinted papers gives less contrast than printing on pure white papers, but because the long and short light rays in ordinary light do not focus well on the retina of the eye, a slightly yellow background is sometimes preferred.[28] Better contrast is obtained on yellow-white (cream) paper than on blue-white paper, when both papers have the same papermaker's brightness. However, the most desirable tint of white depends upon the color of the ink used for printing the paper. Duplicator ink, for example, appears purple on white paper, and much darker, almost black on yellow paper.

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[26] J. H. Bardsley and L. Morin, *Pulp Paper Mag. Canada 48*, No. 3: 159-162, Convention Issue (1947)

[27] R. Buchdahl, M. F. Polglase and H. C. Schwalbe, *Paper Trade J. 122*, No. 18: 143 (May 2, 1946)

Uniformity. The most important property of paper for any printing press is uniformity. The printer can regulate the ink or press to print practically any paper, and so long as the paper is uniform, no trouble will occur. On the other hand, if the paper is non-uniform from lot to lot or sheet to sheet, the quality of the printing will suffer, and in extreme cases, the press may have to be stopped at intervals to adjust the ink or press conditions. Press makeready must be prepared for a paper of definite thickness, and consequently any variation in thickness away from the standard will cause a variation in impression, resulting in poor printing. Ink receptivity, oil absorbency, smoothness, porosity, and other similar properties should also be as uniform as possible, not only from sheet to sheet, but also over the entire area and on both sides of the paper.

If only one side of the paper is to be printed, the felt side is generally used, since this is the smoothest and best printing side. Of minor importance is the fact that printing on the felt side permits the watermark to be read on the same side as the printing is read. If both sides of the paper are to be printed, the wire and felt sides should be as nearly alike as possible to eliminate the difficulties resulting from differences in smoothness. Generally speaking, trouble with two-sidedness is more frequent on machine-finished and supercalendered papers than on coated paper.

Most printing papers for sheet-fed presses are cut machine direction long. After the paper is printed on one side, it is turned over the long way and printed on the reverse side. Thus, the same edges are used for grippers and guides when printing both sides of the paper, and hence no special trimming of the paper is necessary. This method of printing is called work and turn (when the same printing form is used on both sides), or sheetwise (when a different form is used on each side). On special occasions, the paper may be turned over the short way for printing on the reverse side. This method, called tumble, requires special guillotine trimming of the paper, since a different gripper edge is used in each case.

Printing papers should be free from surface fuzz, pronounced felt and wire marks, shives, or too prominent a watermark, since these imperfections impair the quality of the printing. Lumps and grit should be absent, since they are likely to damage the printing plate. According to Strachan,[29] particles about 0.1 to 0.05 mm. in diameter do the most damage to printing plates. Paper for sheet-fed presses must be stiff enough to prevent wrinkling when passing down to the guides and when adjusted to position by the joggers.

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[28] I. H. Godlove and E. R. Laughlin, *Paper Trade J. 111*, No. 17: 216–223 (Oct. 24, 1940)

Some of the troubles which occur in printing can be attributed to paper which has been damaged in manufacture or in shipping. In web printing, pressroom troubles may be due to poorly wound rolls, which develop wrinkles or cause breaks, wrinkled paper, tight or loose edges, or improperly made splices. When printing individual sheets, trouble may be experienced with paper cut out of square, torn sheets, or paper containing mechanical defects. Rough edges may prevent the sheet from coming down to the guides evenly and may cause more than one sheet to be picked up by the feeders at one time.

Smoothness. Printability of paper can be measured by press runs or simulated press runs, as described earlier, but printability can also be evaluated from the individual characteristics of the paper, among the most important of which are smoothness, gloss, formation, finish, ink receptivity, porosity, bulk, hardness, opacity, brightness, and uniformity. One of the most important single properties of paper for relief printing is the smoothness or finish of the paper, because this determines the ease with which the printing plate can be brought into contact with the paper. The printing plate carries an ink film about 3 to 10 microns in thickness, only about one-half of which is transferred to the paper. No contact will be made between the plate and the low spots in the paper if the depressions in the paper are deeper than the thickness of the ink film at the time of impression.

Actually, papers having a wide range of smoothness or finish are used for relief printing, some of the most common finishes on uncoated papers being: (*1*) antique finish, a very soft uncalendered finish used where bulk is important; (*2*) eggshell finish, a dull rough finish which resembles the surface finish on an egg shell; (*3*) machine finish, a fairly smooth finish produced on the paper machine; (*4*) English finish, a dull but smooth finish which is produced on the paper machine; (*5*) supercalendered finish, a very high finish obtained on the supercalenders. The low-finish grades (antique and eggshell) are suitable for type or line illustrations only, it being impossible to obtain faithful reproduction of halftones on such rough surfaces. Medium-finish grades (machine and English) are suitable for the printing of 85- to 100-line screen halftones, whereas the high-finish grades (supercalendered and coated paper) will print fine screen (150 line) halftone illustrations. There is considerable difference of opinion regarding the screen size best adapted to various papers. Papermakers tend to give finer screen values for a given paper than printers do. Table I gives data based upon long-run good printing jobs (press runs of 500,000 to 4,000,000),

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[29] J. Strachan, *Paper-Maker 117,* No. 5: 331–332 (May, 1949)

TABLE I

SUITABLE SCREEN SIZES FOR HALFTONE REPRODUCTION ON VARIOUS PAPERS FOR LONG-RUN PRINTING JOBS BY THE RELIEF PROCESS

Screen size, lines	Type of paper
50–85	News
85–100	Bonds and ledgers, English finish, and machine finish
110	Supercalendered book, although quite a bit of supercalendered book is also printed with 100 screen
120	Machine-coated and brush-coated papers, and sometimes supercalendered paper, when plates from same original are used for both coated and supercalendered papers
133–150	Very special work where fine detail is required on highly finished coated papers

which serve as a guide for production work. English finish papers can take 133-screen printing, but only for high-grade, very short-run work, and not for production operation. Even when printing type, smoothness is a factor in determining the quality of the results. For a given type face, the printing will stand out better and appear heavier when applied to smooth, hard-surfaced papers (e.g., coated or supercalendered papers) than it will on rough, soft-surfaced papers (e.g., antique or machine-finished papers).

If the paper is rougher than desired, the printer may have recourse to one of two alternatives: *(1)* he may use greater printing pressure, or *(2)* he may apply a thicker film of ink. There is a limit to the amount of pressure which can be applied, since high pressure causes mottling and, in extreme cases, causes the printing form to break through the high spots on the paper, resulting in a condition known as "punching." If the paper is too rough, punching occurs before the pressure is sufficient to insure good contact with the low spots of the paper. Increased thickness of ink film improves the intensity or color contrast of ink on the paper, but because more ink is carried on the plate, the ink mileage is reduced, the likelihood of fill-up is increased, and the tendency toward offset is aggravated. Differences as high as 50% in ink mileage can be attributed to differences in the surface characteristics of paper.[30]

The smoothness in which the printer is interested is not the smoothness of the paper under normal unstressed conditions, but rather the smoothness of the paper under the pressure of the printing form. This is called printing smoothness, which might be defined as the proportion of the paper which approaches a smooth surface when the paper is subjected to pressure comparable to that which it receives during printing.[31] Since this pressure

[30] G. Cramer, *Paper Trade J. 114*, No. 12: 146–148 (Mar. 19, 1942)

[31] S. M. Chapman, *Pulp Paper Mag. Canada 48*, No. 3: 140–150, Convention Issue (1947)

may be as high as several hundred pounds per square inch, printing smoothness is determined by the softness and resiliency of the paper at high pressure, as well as the initial smoothness. Softness and resiliency, in combination with smoothness, are better indications of printability than smoothness alone.[32] There are several laboratory instruments[33] for measuring the smoothness of paper under low pressure, but the results do not always agree with results on a commercial press. Chapman[34] believes that a desirable instrument for measuring printing smoothness would be one which measures the fraction of the paper surface which approaches within 0.0001 in. of a smooth surface under a definite pressure approaching the pressure used in printing. For a further discussion of smoothness, the reader is referred to Chapter XVI.

All papers reach perfect printing smoothness if the printing pressure is great enough.[35] The amount of pressure required depends upon the hardness of the paper and the cushion provided.

A soft, resilient paper, even though fairly rough, will print better than a hard paper which is fairly smooth, because the soft paper will act as a cushion under the printing form, whereas the hard paper will remain relatively non-compressible. With soft papers, the wire marks disappear at moderate pressure, whereas very high pressure is required to eliminate the wire marks in hard papers.[36] An indication of the softness of paper can be obtained by measuring the caliper and/or the smoothness of the paper at no load, and under a pressure of about 200 to 250 p.s.i. An indication of the resiliency can be obtained by measuring the thickness after release of the pressure and comparing with the original thickness of the paper.

Calendering of the paper is necessary to obtain the higher finishes required for halftone reproduction. Calendering closes the surface pores of the paper, but does not appreciably affect the rate of internal oil penetration,[37] although it does result in a slight decrease in initial oil absorption. The best printing papers are those which are formed evenly on the paper machine and not calendered excessively, since excessive calendering causes blackening of the paper and produces hard spots which have poor ink receptivity. If hard spots are present in the paper, the ink can be adjusted to increase its penetrating qualities, but this produces a general dulling of the printing.[38] If it is necessary to reproduce fine halftones on rough papers, a small area of the paper may be crushed flat by pressing with a heated brass plate (called hot smashing) and the paper printed in the smoothed area. In general, however, calendered papers are used where halftone reproductions are required, hot smashing being reserved for special effects. The presence of fillers in the paper increases the smoothness, the finer particle size pigments being most effective.[39]

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[32] G. L. Larocque, *Paper Trade J. 106,* No. 26: 368–372 (June 30, 1938)

[33] Bekk Smoothness Tester: Gurley Smoothness Tester; Williams Smoothness Tester (see TAPPI Standards)

[34] S. M. Chapman, *Pulp Paper Mag. Canada 48,* No. 3: 140–150, Convention Issue (1947)

[35] J. H. Bardsley and L. J. Morin, *Paper Ind. 29,* No. 3: 438–440 (June, 1947)

[36] *Idem.*

[37] B. L. Wehmhoff, R. H. Simmons and D. H. Boyce, *Paper Trade J. 96,* No. 4: 48–52 (Jan. 26, 1933)

Ink Receptivity. Ink receptivity is the property which causes paper to accept printing ink at the instant of contact between the paper and the ink. It is a surface phenomenon which is determined by the ease with which the ink wets the paper and by the uniformity and density of the impression obtained when a normal amount of ink is used. The ink receptivity is considered good when the paper accepts the ink readily and uniformly over the whole surface. Ink receptivity is a somewhat different concept from oil absorption and oil penetration. Ink receptivity is primarily concerned with the transfer of ink to the paper, whereas oil absorption and oil penetration are primarily concerned with drying of the printed ink film. Ink receptivity is a function of both the paper and the ink; it is not a property of a particular paper, but rather is a property of paper when tested in combination with a particular ink.

It is difficult to measure ink receptivity independently of oil absorption, and as a result, most tests measure a combined value of the two. A so-called ink receptivity test is sometimes made on paper by smearing a standard ink (K and N ink) on the paper, leaving the ink for a definite period of time, removing the excess ink, and measuring the depth of color. This test is used particularly on coated papers and is discussed further in the chapter on coating. It is best to compare the results with a paper of known ink receptivity.

Another method of measuring a so-called ink receptivity value involves printing a weighed strip of paper with an excess of ink, using a solid plate with an area of 100 sq.cm. The surplus ink on the paper is removed by blotting, and the printed paper is then reweighed to determine the quantity of ink absorbed by the paper. An indication of the ink receptivity can also be obtained from a proofpress run by measuring the amount of ink left on the printing plate. This method is, however, subject to the personal interpretation of the person making the test, and at best is only an indication of the results to be expected in commercial printing.

Because most printing inks have an oil or resin base, oils such as castor oil or petroleum oil are used to measure the ink receptivity and oil absorption. It is helpful to distinguish between (*1*) oil absorption, which refers to the surface penetration of oil and is roughly the same as ink receptivity, and (*2*) oil penetration, which refers to the extent of penetration of oil into the interior of the paper. It is the former, i.e., oil absorption, which is most important in ordinary relief printing, since regular relief inks do not penetrate more than 1 to 7 microns below the surface of the paper. In fact, in halftone printing, the spreading of the halftone dots may be nearly as important as the absorption of ink into the paper.[40]

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[38] G. Cramer, *Paper Trade J. 113,* No. 7: 78–82 (Aug. 14, 1941)

[39] G. L. Larocque, *Paper Trade J. 106,* No. 26: 368–372 (June 30, 1938)

Oil absorption is best evaluated by the initial resistance of the paper to the break through of oil.[41, 42] In one test, a drop of castor oil or a standard mineral oil (SAE 20) is placed on the paper and quickly spread into a thin film by pulling the paper under a weighted rubber roller which exerts a definite pressure (i.e., 2 lb.) on the paper. The time is taken for the initial break of the oil film, as evidenced by a 75% loss in sheen. In a variation of this test, a drop of heavy white mineral oil is placed on the surface of the paper or paperboard and spread into a thin film by allowing a heavy 8-lb. roller to run down a 1 to 50 inclined plane over the drop of oil. The time is taken for the partial absorption of the oil into the paper or paperboard. A special photometer is used to measure the end point which is taken as either the time required for a 50% reduction in the gloss of the oil film or as the gloss after a definite time has elapsed, i.e., twenty seconds.[43]

Another test sometimes used for measuring the resistance of paperboard to ink is the butyl carbitol test in which the time is taken for the complete absorption of one drop of butyl carbitol (diethyleneglycol monobutyl ether) applied to the paper from a tube located 3 in. above the sample and calibrated to deliver at the rate of one drop per second. The butyl carbitol should contain a small amount of water so that it is in equilibrium with the atmosphere.

The results obtained with the above tests serve as a rough guide to the printing qualities of the paper. Too low an oil absorbency indicates that the ink will be slow in drying and will tend to set-off on the back of the next printed sheet (offset). Too high an oil absorbency means that the vehicle of the ink will be carried too far into the paper. This causes a loss of opacity and, in extreme cases, results in staining of the back side of the sheet. The proper absorbency for the paper is governed by the type of ink used. Papers such as bonds, ledgers, and coated grades are generally printed with inks which dry mostly by oxidation, and hence a relatively low degree of absorbency is desired. Papers such as machine-finished and supercalendered book are generally printed with inks which dry partly by absorption

[40] R. M. Cobb and D. V. Lowe, *Paper Trade J. 98,* No. 12: 151–153 (Mar. 22, 1934)

[41] G. L. Larocque, *Paper Trade J. 106,* No. 26: 368–372 (June 30, 1938)

[42] V. V. Vallandigham, *Paper Mill News 68,* No. 52: 10–16 (Dec. 22, 1945)

[43] V. V. Vallandigham, *Tech. Assoc. Papers 29:* 523–525 (June, 1946)

and partly by oxidation, and hence a higher degree of absorbency is desired. Papers and paperboards to be printed with high gloss inks require a very low absorbency, and these papers are generally surface-sized with starch, carboxymethylcellulose, or similar sizing agents to produce an oil-resistant surface.

The oil absorbency of paper is decreased by increased calendering, reduced filler content, and increased density. In filled papers, the oil absorbency is generally higher on the felt side because of the greater concentration of filler on that side of the paper.[44] Because of this higher oil absorbency, a slightly greater amount of ink must be carried on the printing plate when printing the felt side of the paper.

Surface Bonding Strength. The surface bonding strength is an important property of printing papers. Poor bonding results in picking (a lifting of the surface coating or fibers away from the body of the paper) or, in more extreme cases, body stock splitting. Picking of inked fibers off the surface of the paper leaves a white spot on the surface of the paper where ink should be. The loosened fibers may clog the type, contaminate the ink, and eventually show up on a subsequent sheet as an inked spot surrounded by a white ring.

Picking frequently occurs with poorly sized machine-finished book papers, the felt side being more likely to give trouble than the wire side. Like most printers' problems, picking can be caused by a number of different conditions, for example, weak paper, faulty press, poor makeready, or too tacky an ink (see section "Pressroom Difficulties"). Another trouble resulting from too soft a paper is linting or dusting, which is particularly prevalent when the cutter knives are dull.

Beating increases the bonding strength of the paper and reduces picking troubles. However, paper for relief printing should be made with the minimum amount of beating and jordaning necessary to obtain proper formation and minimum picking, since excessive beating builds up internal strain in the paper, reduces the softness and resiliency, and reduces oil penetration. Increasing the basis weight is of no value in reducing picking troubles, since this does not increase the amount of fiber bonding. Starch and glue sizing improve bonding. Fillers improve the over-all printability, but excessive amounts of filler are likely to cause trouble with picking and dusting during printing.

Opacity. Paper for printing should have high opacity in order to prevent show through of printing on the back of the printed sheet. Show through is most apparent when halftones or solids are printed on one side of the paper and type on the other.

A high original opacity is helpful in preventing show through, but it is no guarantee against its occurrence, since the original opacity of the paper may be reduced by excessive penetration of oily vehicle into the paper. This occurs when the paper has a high oil absorbency and is most prevalent in the case of low-finish book papers, newsprint, and mimeograph papers. Fillers such as clay increase the original opacity of the paper and are ordinarily considered to reduce show through, but clay has relatively little opacifying effect in the presence of the ink vehicle and may actually increase show through by increasing the oil absorbency of the paper.[45] High-opacity fillers, e.g., titanium dioxide, are much more effective than clay.

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[44] M. S. Kantrowitz, *Paper Trade J. 128,* No. 25: 231–234 (June 23, 1949)

The tendency of printing papers to exhibit show through can be measured by the printed opacity test. In this test, the sample of paper is printed in a solid black and then the opacity is measured, using the back of the sheet. This test takes into account the degree of penetration of ink into the paper, as well as the original opacity of the paper. The subject of opacity is discussed further in Chapter XVI.

Effect of Moisture and *p*H in Papers for Relief Printing. Moisture content affects the strength, dimensional stability, ink receptivity, finish, softness, and all-round printing qualities of paper. Control of the moisture in printing papers is essential for the control of register, curling, creasing, static electricity, and cockling. The optimum moisture content for papers for ordinary relief printing is about 4.5 to 5.5%.[46, 47]

Too low a moisture content results in a hard, brittle paper with poor printing qualities. Damp paper prints better than dry paper, due to its greater resiliency which causes the paper to flatten out better under the printing pressure. Many years ago, it was the practice, for high-quality relief printing, to dampen the paper before printing. (In copper and steel engraving, the work is still wet before printing.) Excess static and trouble with curl result when the moisture content is too low. If the moisture content is less than about 4%, the paper will lose considerable strength when printed with heat-set inks.

Too high a moisture content leads to loss of finish, misregister, cockling, and curl, and if heat-set inks are used, to blistering. Excessive moisture has an inhibiting effect on the drying of the ink, drying time increasing in direct proportion to the moisture content of the paper.[48] Drying of the ink is generally retarded by a very low or by a very high *p*H of the paper, although the source of the alkalinity must be considered. A *p*H around 5.0 is probably best.

The moisture content of paper for printing can be measured very simply by means of a special hygrometer, called a "sword." This instrument, after it has been calibrated against a sling psychrometer, is inserted between the sheets of paper and held there until a steady reading is obtained. The moisture content is obtained from tables similar to Tabel II.

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[45] U. S. Government Printing Office, Tech. Bulletin No. 18, "Newsprint and News Ink" (1933)

[46] M. J. Leckey, *Paper Trade J. 116*, No. 20: 223–226 (May 20, 1943)

[47] H. H. Slater, *Printing Equipment Engr. 70*, No. 5: 84–86 (Aug., 1945)

[48] M. J. Leckey, *Paper Trade J. 116*, No. 20: 223–226 (May 20, 1943)

TABLE II

RELATION BETWEEN READING OBTAINED WITH SWORD HYGROMETER AND MOISTURE IN PAPER

Humidity, %	Moisture, %
26	4.0
36	5.0
47	6.0
59	7.0

Static Electricity. Static electricity may be generated by paper rubbing against metal, wood, or other sheets of paper. Static develops most frequently under conditions of low relative humidity of the atmosphere (i.e., below about 50%), when the paper has a low moisture content (i.e., below 3½% moisture), when the paper has a high finish, and when the paper has lower temperature than the pressroom. Static electricity has become more of a problem as operating speeds have increased.

Some of the undesirable conditions developed as a result of excessive static electricity are: (*1*) fine specks of foreign matter (e.g., paper dust) are attracted to and held on the surface of the paper; (*2*) the paper sticks together, causing difficulties in feeding and register and resulting in offset on the printed sheets. Spraying or misting of ink is said to be the result of static built up in the ink from the break away of the rollers. Controlled polarities have been utilized in the electronographic press to print with a gap of 0.001 in. between the printing surface and the paper.

Static electricity can be controlled by grounding the paper with tinsel cord which makes contact with the paper as it comes off the press. It can be minimized by keeping the relative humidity of the pressroom as high as possible. Paper having a high moisture content is less likely to develop static electricity and, if it does, it can be discharged readily by grounding, since the conductivity increases at high moisture content. Warming the paper helps to reduce static electricity. A method of discharging static is to pass the paper through a localized alternating ionized field as it comes off the impression cylinder on the way to the delivery table.[49]

Coated Papers for Relief Printing

Coated papers are widely used in relief printing for the reproduction of fine halftone illustration. Both regular coated and machine-coated papers are used, machine-coated papers having replaced supercalendered papers to a large extent.

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[49] M. S. Pennell, *Paper Trade J. 130*, No. 15: 33–37 (Apr. 13, 1950)

One advantage of coated paper over uncoated paper lies in the greater surface smoothness obtained from the mineral coating, which overcomes the high and low spots found in ordinary printing papers. The increased smoothness of coated paper means that less pressure is required in printing and less ink need be carried on the printing plate. For example, Bekk[50] found on a laboratory press that a given degree of blackness was obtained on coated paper when only 1.38 g. of ink per square meter was carried on the press compared with 2.60 g. for newsprint. However, the greatest advantage of coated paper is that the coating layer furnishes a printing surface which is far more uniform in density and oil absorption than any uncoated paper surface, however smooth. Massey[51] states that the ideal printing paper is the one which most closely approximates a 100% mineral surface.

By far the biggest difficulty with coated papers is the tendency for the coating to pick from the surface of the paper, thereby resulting in an unattractive printing and contaminating the ink with bits of coating. The basic cause of picking is too tacky an ink, but picking can be the fault of insufficient binder in the coating. When ink is applied to the surface of the paper, part of the ink transfers to the paper and part remains on the printing plate. The pull resistance or tack of the ink exerts a force on the paper, and it is the relationship between this pull resistance of the ink, the adhesion between the ink and the coating, and the strength of the coated paper which determines the tendency to pick. If the pull resistance is less than the strength of the coating and the paper, no picking occurs. However, if the bond between the paper and the coating is weaker than the pull resistance of the ink, or if the bond between the individual pigment particles in the coating layer is weaker, or if the coating is strong enough but the paper itself is weaker, picking will occur. The first two types are called coating pick, and the last is called a body stock pick. Picking may result from breaking of the coating in handling (by bending). This is not due to weak coating or body stock.

The tendency of an ink to pick is a relatively fundamental property of the ink. However, the pull resistance of the ink increases with the speed of printing and with a reduction in the thickness of the ink film.[52] Hence, picking can sometimes be reduced by slowing down the press or by increasing the thickness of the ink film. The most common remedy for picking is to reduce the tack of the ink by adding waxes or thinners, but this has the disadvantage of lowering the printing quality (see section "Pressroom Difficulties").

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[50] J. Bekk, *Textil-Rundschau 1*, 3: 75–78 (Sept., 1946) through *B. I. P. C. 17*, 12: 717–718 (Aug., 1947)

[51] P. J. Massey, *Paper Trade J. 109*, No. 16: 210–213 (Oct. 19, 1939)

[52] R. F. Reed, *Paper Trade J. 102*, No. 22: 281–283 (May 28, 1936)

Cracking of the coating, which is sometimes confused with picking, frequently occurs on heavily coated papers which are printed under so much pressure that the coating is broken. Cracking occurs if the paper loses its pliability as a result of low humidity, which is most likely to happen in the winter months. Other difficulties with coated papers arise from imperfections in the coated surface, such as those due to pinholes, "fish eyes," brush marks, roll marks, dirt specks, or lumps of undispersed adhesive and pigment.

Most coated papers have good ink receptivity and clean the printing plate almost perfectly. However, some coated papers have low ink receptivity and result in the accumulation of ink on the printing plate, leading to messy printing. The amount and type of adhesive used in the coating is the principal factor affecting the ink receptivity, although certain pigments (e.g., calcium carbonate and satin white) improve this property. Too much adhesive in the coating results in a coating which is hard and does not lift the ink cleanly from the printing plate, and the ink which is transferred to the paper is slow in drying. However, hard-finished coated papers may be desirable where the printing must be non-scratch. Starch is generally considered as a soft adhesive but starch-coated papers may be harder than casein-coated papers because of the greater amount of adhesive required in the coating. Machine-coated papers sometimes contain stearates and other soaps (added to overcome dusting and improve the leveling properties), and if excessive amounts of these materials are present in the coating, drying of the ink may be greatly retarded.[53] The ink can be adjusted to increase the pick-up by reducing the cohesiveness, but this has a tendency to make the ink too short. Cast-coated papers are highly ink receptive but friction-glazed papers have a hard, waxy surface which is quite ink-resistant.

With some coated papers, the opposite trouble from that described above is encountered, namely, the coating has too high an oil absorption and tends to rob the ink of binder, with the result that the ink chalks. A delicate balance must be maintained, and consequently the drying of inks on coated paper is more of a problem than it is on uncoated paper. The correct amount of binder for a particular coated paper can be determined only by trial and error, but the Dennison wax and oil absorption tests can be used as a guide. In general, coated papers for ordinary relief printing should pass a Dennison wax of 4, but should be no stronger than a Dennison wax of 6 to 7. The minimum pick resistance for coated two-side paper

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[53] M. J. Leckey, *Paper Trade J. 116,* No. 20: 223–226 (May 20, 1943)

TABLE III

MINIMUM PICK RESISTANCE FOR COATED PAPER PRINTED BY RELIEF PROCESS ON SINGLE-COLOR PRESS

Type of printing	Dennison wax	Inkometer
Halftone—few solids	5	7
Tint blocks and halftones	6	12
Gloss ink—light form	6	12
Gloss ink—heavy form	7	20

for relief printing on a single-color press is shown in Table III.[54] Using a proofpress, Bowles[55] found that absorbent coatings resulted in serious mottle, whereas non-absorbent coatings resulted in little or no mottle when inks of low pigmentation were used.

Paperboard for Relief Printing

A considerable amount of paperboard is printed by the relief process, and the problems are much the same as those in the printing of paper. There are, however, a few special precautions to observe. Paperboards are often scored and folded, which means that the ink film must be fairly rubproof. Scuff-proofness is required for resistance to rub during shipping. If the board is to be used for the packaging of foodstuffs, particular care must be taken to select odorless inks. Inks with a drying oil base tend to have a bad odor unless special care is taken in the formulation of the ink.

Printing inks must be adapted to the type of board, for example, white patent coated board cannot be printed satisfactorily with an ink designed for chipboard. Sulfite and sulfate-lined paperboards do not print with the same ease. As a rule, jute board (board lined with waste kraft) prints more easily than solid virgin kraft board, primarily because of its greater smoothness and better ink receptivity.

Much paperboard is printed with high-gloss inks which dry to a hard, glossy film. Gloss inks dry mainly by evaporation and oxidation of the vehicle with a minimum of penetration, and hence paperboard for gloss ink printing must have a high resistance to ink penetration. It is for this reason that paperboard for gloss ink printing is usually calender-sized with starch, algin, methylcellulose, or carboxymethylcellulose. In some cases, paperboard may be overprinted with varnish to increase the gloss and protect the surface of the board against scuffing.

A special process sometimes used for printing the outside liner of corrugated and solid fiber paperboard utilizes a relatively cheap aqueous ink made with casein, alkali, and dyestuffs. The casein acts as a binder for the dye and imparts water resistance to the ink so that it will not be washed

[54] F. A. Weymouth, *Paper Trade J. 130*, No. 24: 118–121 (June 15, 1950)

[55] R. F. Bowles, *Penrose Annual 42*, 153 (1940)

off in handling. Starch treated with urea-formaldehyde resin has also been used in this process with some success. The press consists of two rolls, a metal engraved roll for applying the ink and a rubber impression roll for pressing the paper against the printing roll.

Printing with Aniline Inks

Aniline printing is a variation of the relief process, which uses a rotary press equipped with rubber plates to print paper continuously in web form. Aniline printing is widely used when the paper is to be printed and converted in continuous operation, e.g., when making bread wrap. An aniline press is a relatively simple press consisting of a motor-driven impression cylinder, a plate cylinder, and ink fountains. Rubber ink rollers and rubber plates are generally used. The fountains can be backed away from the plate, or the plate and fountains can be backed away from the impression cylinder, using hand wheels.

Aniline inks are composed of organic dyestuffs dissolved in solvents such as alcohols, ethers, ketones, esters, or ether-alcohols, basic dyes being generally used because of their brilliance. The ink contains a resinous binder (e.g., shellac, gum copal, ester gum, phenolic resin, special rosin-type maleic resins, vinyl acetate resins, nitrocellulose, glyptal, or manila gum) which serves to add body to the ink and to act as a binding agent for holding the ink on the paper. Pigments such as titanium dioxide are sometimes added for opacity, particularly when the ink is to be used on transparent papers. Many other compositions may be used.

Aniline inks dry principally by evaporation, sometimes with the aid of gas, electrically heated driers, or infrared lamps. Because of their rapid drying, aniline inks are used for the printing of non-absorbent stocks. When printing moistureproof cellophane or dry waxed papers, a small amount of ethylene dichloride may be added to the ink to increase the wetting. Special drying apparatus is generally required when printing moistureproof cellophane. Gas drying with intense heat is best, since it is quick enough to prevent detrimental action to the stock.[56] Paper bags, Christmas wrappings, bread wrapping, paper milk containers, metal foil wraps, and gummed tapes are grades sometimes printed with aniline inks. These papers are generally fabricated on fast machines where the rapid-drying properties of aniline inks are advantageous in permitting handling of the paper immediately after printing.

Printing of Newsprint

The printing of newsprint is a special type of relief printing. Newsprint is generally printed in roll form on rotary presses at very high speeds.

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[56] R. M. Bates, *Paper Trade J. 104,* No. 13: 192–195 (Apr. 1, 1937)

No bearers are required, and the impression cylinder packing is quite soft. Some weekly newspapers are printed on flat-bed presses in a sheet size of 30½ × 44 in.

Newsprint is generally printed with a special, non-drying black ink, called news ink. The ink consists of a simple mixture of mineral oil (semi-refined naphthenic or paraffinic base petroleum oil) and about 13% carbon black. A cheap resin (e.g., rosin) may be present in the ink to increase the tack, improve the wetting qualities, and increase the hardness of the ink film. Toners (black dyes dissolved in oleic acid) may also be present.

There is no drying of news ink in the sense that ordinary printing inks dry, since news ink dries entirely by penetration, the ink being attracted into the pores of the paper by capillary forces and retained there in the form of a soft, easily smudged film. The absorption, or so-called drying, of news ink depends upon the absorbency of the paper, the viscosity of the ink, the moisture content of the paper, and the relative humidity of the atmosphere. The rate of drying is an inverse function of the square root of the ink viscosity.[57] Because of the high speed of news presses (800–1500 f.p.m.), there is only a relatively short time during which the ink must be absorbed by the paper. When operating at high speed, the paper is in contact with the plate for about 1/1000 of a second, and 1/10 to 2/5 of a second later the reverse side of the paper is printed.[58, 59] Hence, rapid drying of the ink is an essential requirement in newspaper printing.

The surface oil absorption test, in which the time is taken for the absorption of a thin film of oil into the paper, bears no relation to the total or internal oil penetration,[60] and hence this test is not well suited for the evaluation of newsprint and other porous papers (e.g., mimeograph). For these porous papers, the rate of penetration of oil into the interior of the paper is a better criterion of the printing qualities than the surface absorbency. In measuring oil penetration, a drop of castor oil is placed on the paper and (*1*) the time is taken for the complete absorption of the drop, or (*2*) the time is taken for the paper to become translucent. The rate of penetration is logarithmic in nature.[61] The rate is directly proportional to the viscosity of the oil,[62] and, as would be expected, is inversely proportional to the temperature of the oil between 25 and 35° C.[63] In general, high oil absorbency is desired, lack of absorbency being the most common shortcoming of newsprint.[64] Too high oil absorbency, however, results in strike through of ink vehicle.

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[57] A. De Waele, *J. Am. Chem. Soc. 48:* 2760–2776 (Nov., 1926)

[58] G. Larocque, *Pulp Paper Mag. Canada 48,* No. 3: 94–99, Convention Issue (1947)

[59] W. G. Forster, *TAPPI Bulletin* No. 80 (Aug. 11, 1947)

[60] G. L. Larocque, *Pulp Paper Mag. Canada 38:* 77–84, Convention Issue (1937)

[61] V. V. Vallandigham, *Paper Mill News 68,* No. 52: 10–16 (Dec. 22, 1945)

[62] "Instrumentation Studies," *Paper Trade J. 110,* No. 4: 44–50 (Jan. 25, 1940)

[63] H. H. Grantham and W. Ure, *Paper Trade J. 101,* No. 12: 143–147 (Sept. 19, 1935)

Like all printing papers, newsprint should have a smooth surface, high opacity, and uniform formation, and although newsprint is generally inferior to other printing papers in these respects, improvements have been made in recent years. The finish is generally a machine finish, a higher finish being preferred by English than by American newspapers. The higher the smoothness, the lower the oil absorbency. The oil absorbency is greater on the wire side than on the felt side because of the lower smoothness on the wire side.[65, 66]

Newsprint is generally made unsized, although a small amount of alum may be added. There is little or no mineral loading, the ash generally being less than 2%, although in some cases, about 4 to 5% calcium carbonate may be used to improve the oil absorbency. (Because a large quantity of American newsprint is imported, the amount of sizing and loading in standard newsprint paper has been defined by the United States Customs Court and Treasury Department in such a way as to prevent its competition with other printing papers.) The basis weight varies from 30 to 35 lb. (24 × 36—500), 32-lb. newsprint being most common. High moisture content (e.g., 10 to 12%) reduces the danger of breaks on the machine,[67] but a lower moisture (e.g., 4 to 6%) is most desirable from the standpoint of faster drying of the ink. High bulk is desirable. The per cent bulk as measured by calipering four sheets and dividing by the weight of the paper varies from about 75 to 98%, 82% being an average.[68]

The standard furnish for newsprint is 80 to 85% spruce groundwood and 15 to 20% unbleached spruce sulfite. Groundwood adds the desirable properties of high opacity, smooth surface, and high oil absorption.[69, 70] Sulfite adds the necessary strength required to get the paper through the press without breaks. The cause of breaks is not so much a lack of tensile strength as it is a lack of elasticity of the paper, since the tensile strength in the machine direction is about 11 lb. per inch of width, compared with the average pull on the paper in the press of about 0.5 to 1.0 lb. per inch.[71]

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[64] G. Larocque, *Pulp Paper Mag. Canada 48,* No. 3: 94–99, Convention Issue (1947)

[65] H. H. Grantham and W. Ure, *Paper Trade J. 101,* No. 12: 143–147 (Sept. 19, 1935)

[66] A. Voet and J. S. Brand, *Paper Trade J. 122,* No. 24: 264–269 (June 13, 1946)

[67] J. P. Grant, *Pulp Paper Mag. Canada 46,* No. 3: 149–151 (Feb., 1945)

[68] A. T. Gardner, *Pulp Paper Mag. Canada 46:* 78–79 (Aug., 1946)

[69] U. S. Government Printing Office, Tech. Bulletin No. 18, "Newsprint and News Ink" (1933)

[70] H. H. Grantham and W. Ure, *Paper Trade J. 101,* No. 12: 143–147 (Sept. 19, 1935)

[71] U. S. Government Printing Office, Tech. Bulletin No. 18, "Newsprint and News Ink" (1933)

Some of the other causes of breaks are insufficient moisture in the paper, poorly wound rolls, slime spots, thin spots, lumps, and calender cuts. Owing to the loss of strength which occurs on aging, newsprint prints better when it is less than six months old.[71a]

Intaglio Process

Intaglio printing consists of printing from an engraved or recessed surface, which is the reverse of the relief process. In the intaglio process, the plate is inked by rollers, the excess ink removed from the unetched surface of the plate, and the paper is then pressed against the plate where it picks up the ink held in the recessed areas of the plate. There are several types of intaglio printing, among the most important of which are copper and steel engraving, sheet-fed gravure printing (photogravure), and rotogravure.

Copper and Steel Engraving

In engraving, printing is done from flat steel or copper plates, using short, buttery inks. The plate is inked, wiped with a cloth, a sheet of paper is placed on the plate, and the plate and paper assembly is then passed under heavy rollers.

Pictorial designs can be obtained in engraving by cutting out fine lines or dots in reverse directly on a copper plate, using a steel cutting tool. Etched plates can be made by scratching the design on a wax coating on the surface of the plate, using a fine needle, apd then removing the exposed metal in an acid bath.

The results obtained by engraving are very artistic and individual in their effect, but the process is slow and expensive. Copper plates are relatively soft and are suitable only for a few thousand impressions, after which the printing loses its sharpness. Because of the high cost and limited production, engraving is used mostly for the printing of letterheads, banknotes, social stationery, bonds, and for some illustrations where exceedingly fine and delicate lines are desired. In one process, referred to as die stamping, the printing is done at very high pressures to emboss the paper partially. This process is used mostly for letterheads, name cards, wedding invitations, and greeting cards. Special shading effects can be obtained in engraving by graining of the plate surface with hand tools. These processes, known as aquatint and mezzotint, are used only for hand printing of special editions.

Inks for engraving may be of the drying oil type or of the solvent type formulated with a resin and suitable solvents. Solvent inks are made by dissolving resins such as nitrocellulose, maleic resins, vinyl acetate resin, gilsonite, or natural resins in solvents such as xylol, toluol, and high-boiling mineral thinners. Generally, the inks are very stiff so that they will hold in place on the paper. Color strength is not so important as it is in relief printing, since relatively thick films of ink are applied.

[71a] G. Larocque, *Tappi 34*, No. 1: 86A (Jan., 1951)

Rotogravure

Rotogravure is a variation of the intaglio process adapted to high-speed rotary web press printing. Printing is done from copper cylinders or from copper plates fitted to permanent plate cylinders; chromium-plated plates are used for long runs. The design is placed on the printing plate photographically, the process being in reality a rotary-photogravure process, the name having been shortened to rotogravure. In addition to its regular use in the printing of Sunday newspaper supplements, rotogravure printing is also used for wrapping and magazine papers and for the printing of mail order catalogues. Rotogravure is the most important of the intaglio printing processes. It is economical for long runs but is not suited for short runs because of the high first cost of preparing the cylinders.

In preparing illustrations for rotogravure printing, a negative is first made, and from this a transparent positive is obtained on sensitized transparent film. Type matter is made from a glassine paper proof. The positives are printed photographically on a thin sheet of sensitized gelatin-coated carbon tissue paper. First, however, a fine reversed line screen (usually 150-line) is used to put a screen on the carbon paper by passing strong light through the screen onto the paper. The screen is the reverse of an ordinary halftone screen in that the lines are transparent and the in-between areas are opaque. After exposure to the screen, the gelatin-coated carbon tissue is then exposed to the positive film and glassine prints. This hardens the coating on the carbon tissue in proportion to the amount of light which comes through, which means that the gelatin is hardened least in the shadow areas and to the greatest degree in the highlight areas. The gelatin remains soft in those areas corresponding to the lines on the screen.

After exposure, the carbon paper is wetted with water and squeegeed onto a polished copper cylinder, gelatin-coated side against the cylinder. After drying, the back of the paper is moistened with water, and the paper is removed. The soft gelatin is removed with the paper, but the light-hardened gelatin remains on the cylinder, leaving a multitude of little gelatin squares of varying thickness and hardness adhering to the cylinder. The thickness of the squares adhering to the copper cylinder is least in the dark tones and greatest in the light tones. The cylinder is then washed and etched with ferric perchloride which eats into the copper to a depth depending upon the thickness of the gelatin on the cylinder. The deepest etching corresponds to the darkest printing areas. No etching takes place where the screen lines are located, because they are protected by painting with asphaltum before etching. These screen lines function on the finished plate to support the doctor blade and prevent the blade from scraping the ink out of the etched areas.

Ink is applied to the cylinder during printing by means of an ink roller which revolves in an ink bath. A doctor blade scrapes all the ink from the smooth part of the cylinder, leaving ink only in the engraved portions of the cylinder. The paper web is pressed against the cylinder by means of a rubber-covered impression roll which causes the paper to pick up the ink from the recesses in the cylinder. Very thin inks are used, since the ink must flow readily into the recesses of the cylinder and must penetrate the paper very quickly because of the very high-speed press used. The ink dries on the paper mainly by evaporation and only slightly by penetration.

Rotogravure plates differ from relief halftone plates in that all the dots are of uniform size and shape and are closer together than the usual relief halftone. Tone is obtained by differences in the depth of the cups or etching, which determines the thickness of the dots of ink transferred to the paper. One notable difference which distinguishes rotogravure printing from relief (and planographic) printing is that all type and line illustrations, as well as other illustrative matter, may be screened. The ink tends to spread slightly on the paper, which results in a lack of fine detail, but produces a very soft, even, almost continuous printing. Because of this spreading, the screen in rotogravure printing is not so apparent as it is in other processes. The printing area is about 60% and this results in approximately 75% coverage of the paper due to ink spread.[71b]

Sheet-Fed Gravure Printing (Photogravure)

In contrast to the hand work used in copper or steel engraving, it is possible to place the design on the printing plate photographically. Pictorial matter for sheet-fed gravure printing of book illustrations is generally prepared in this way, using a process similar to that used in rotogravure. As in rotogravure, tone is obtained by differences in the depth of etching, rather than by the size of the halftone dots.

In addition to the regular (screen) effects obtained by the above method, it is possible to obtain an irregular or grain effect for special book illustrations. This is done by coating the plate with resin dust and heating to melt partially the resin particles. A transparent positive overlay on carbon tissue is then placed on the plate and the plate is developed. The developed plate is then etched in ferric perchloride. The dust adhering to the plate furnishes the grained effect.

Paper for Intaglio Printing

During printing by the intaglio process, the paper is partially squeezed into the recessed areas of the plate where it picks up the ink. Paper for intaglio printing need not have the high smoothness required for relief printing, but it should have a fairly smooth surface to permit uniform contact with the printing surface. The body of the paper must be soft and resilient to permit its being pressed into the recessed areas of the plate; paper for engraving is frequently moistened before printing. The surface fibers must be well bonded so that there will be no fuzz to fill in the plate. The paper must be reasonably opaque in order to prevent show through, but it must not contain gritty fillers which tend to scratch the polished surface of the printing plate.

[71b] F. B. Johnson, *Tappi 34,* No. 1: 82A–86A (Jan., 1951)

In rotogravure, the paper should have most of the above requirements, but since very thin inks are used in contrast to the stiff inks used in engraving, drying of the ink is not a problem. Supercalendered papers made from groundwood and chemical pulp are most frequently used for rotogravure in weights from 35 to 70 lb. (25 × 38—500). Coated papers are sometimes used, although coating is not necessary. If coated papers are used, they should have the highest resilience possible and should be free of abrasive materials which might scratch the polished non-printing areas of the plate, causing them to print fine lines on the paper. Uncoated papers made from sulfite pulp sometimes cause tarnishing of the mirror finish copper cylinder due to sulfur compounds which may be present.

Planographic (Lithographic) Process

Planographic (lithographic) printing differs from relief and intaglio printing in that the printing ink is carried on substantially the same level as the plate surface, and not upon a raised or recessed surface. Certain areas of the plate are made ink-receptive, and certain areas are kept ink-repellent, the difference between image and non-image areas being obtained chemically, instead of by differences in height of plate. Water containing a small amount of acid is used for moistening the plate during printing to keep the non-printing areas ink-repellent. There is a type of lithography known as dry lithography, but so far this has not been very successful because of the extremely close tolerances which are required.

In order to understand planographic printing, it is necessary to know something about the preparation of the printing plate and the reactions which take place during printing. Planographic printing is a real art because of the many variables involved, but the basic operations should be understood by every paper chemist who works with paper for the planographic process. Two principal types of printing plates are used, albumen plates and deep-etch plates. The method of preparing these plates, as well as the earlier stone plates, are discussed in the following sections.

Printing from Stone

The principle of lithography was discovered by Senefelder in Munich in 1798 while trying to make etchings on limestone. For many years after Senefelder's discovery, lithography was done with a special porous limestone.

In preparing a stone for lithography, the stone was first ground flat and then grained by rubbing with an abrasive such as ground glass. The image was then drawn on the stone in reverse, using a waxy crayon or ink. After the ink was hardened by an acid treatment, the exposed areas of the stone were etched or desensitized by treating with an etch containing gum arabic acidified with nitric acid. The gum arabic was adsorbed and absorbed into the pores of the stone where it acted to keep the non-image areas clean. Finally, the stone was washed in water to remove the acid. The final result was a stone which was receptive to ink in the image areas, but repellent to ink in the non-image areas where water was carried in the pores of the stone. In later years, transfer papers were used for transferring subject matter to the stone, which eliminated the necessity of drawing the image in reverse. Printing from stone is practically a thing of the past, although it is still used for specialty jobs.

Printing from Metal Plates

Modern planographic printing is done from aluminum or zinc plates and, more recently, from bimetallic and trimetallic plates of stainless steel or aluminum coated with a very thin film of copper or copper and chromium. The metal plate is specially grained with hard abrasives (e.g., aluminum oxide or silicon carbide) to imitate the texture of the limestone used by the early lithographers. Graining is necessary so that the plate will absorb water in the non-printing areas of the plate and absorb ink in the printing areas. The grain provides an anchorage for the light-hardened image used in the printing areas.

Planographic printing differs from relief printing in that all art work is photographed by the lithographer at the printing plant, whereas in relief printing, the art work is usually sent to a photoengraver to have the original plates made. On the other hand, type is not set by the lithographer, but instead he usually buys proofs of type from a trade house where type is set. The various steps include setting the type, pulling the proof, photographing the proof, and stripping into the form. A phototypesetter sets type in strips similar to the linotype except that a photographic negative is obtained. In the albumen process, the lithographer reproduces the type photographically from a negative prepared from a paper proof of the type. In the deep-etch process, the lithographer reproduces the type from a positive made from a transparent (cellophane) proof of the type. Under certain conditions (work up to 200-line screen), it is possible to convert a printed proof to a negative and then to a positive for preparing deep-etch plates.[72]

The last step in lithography before preparing the plate is stripping, in which the negatives (or positives) are pasted onto a layout using goldenrod coated paper for the albumen process and cellulose acetate sheeting for the deep-etch process. Once a lithograph plate is made, changes cannot be made on the press, as in relief printing. All changes must be made on the negatives (or positives, in the deep-etch process) before the plates are made.

Printing from Albumen Plates (Photolithography). In the albumen process, the plate, after graining, is cleaned (counter-etched) in dilute acetic acid and then coated with a light-sensitive mixture (egg albumen, water, and ammonium bichromate) and dried. An image is then made on the sensitized plate by exposing the plate under a photographic negative, to strong light from an arc lamp. After exposure, the plate is treated with developing ink and then is washed with water to remove the unhardened albumen coating which carries the developing ink from the non-printing areas of the plate. The printing areas of the plate are the light-hardened areas of albumen which retain the developing ink, whereas the non-printing areas are the exposed regions of the metal plate. As a final step, the plate is gummed to deposit a thin film of gum arabic in the exposed regions of the non-printing areas.

During printing, the non-image areas of the plate are kept wet with an acidified aqueous solution of gum arabic, while the work areas of the plate are kept wet with printing ink. The gum arabic solution is attracted to the exposed areas of the grained metal plate where it is held in the pores, while the ink is attracted to the albumen image. The ink and water are prevented from mixing by their natural immiscibility. The *p*H of the dampening solution must be maintained within certain limits to maintain a stable film of gum arabic on the non-printing areas of the plate and to keep the plate clean by dissolving a slight amount of metal.[73] The optimum *p*H for satisfactory cleaning of the plate surface is about 3.8. If operating conditions make it necessary to lower the *p*H beyond this point in order to keep the plate clean, the albumen image will tend to swell, causing distortion or blinding of the image, and the halftone dots will be undermined, causing sharpening of the image.

Printing by Deep-Etch Process. Deep-etch printing is the most important of the planographic printing processes. The plates used in deep-etch printing last longer than albumen plates, and they print with sharper detail. A bimetallic offset plate can print up to 1,000,000 impressions, which is comparable to the number of impressions obtainable from a relief plate.

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[72] *Modern Lithography 157*, No. 1: 77–78 (Jan., 1947)

[73] F. Kendall, *Modern Lithography* (Mar., 1942)

In deep-etch printing, the printing image is chemically etched a few thousandths of an inch below the surface of the plate so that the process is, in reality, a compromise between gravure and true planographic printing. In preparing a deep-etch plate, the grained plate is first cleaned (counter-etched) and then coated with a light-sensitive coating consisting of dichromated gum arabic. An image is then printed on the dried coating by passing strong light from a carbon arc lamp through a corrected positive which hardens the coating in the non-work areas of the plate. The printed plate is then developed in special developer solution containing lactic acid for about three minutes to dissolve the image and expose the metal in the work areas of the plate. Thus, in the deep-etch process, the coating on the non-printing areas of the plate is hardened, which is the reverse of the situation in preparing an albumen plate. This light-hardened coating then acts as a stencil, so that the exposed work areas of the plate can be etched by a solution which attacks the metal. The etching is rather shallow (usually from 0.0002 to 0.0003 in.) and, in fact, deep etching consists of little more than removing the grain peaks on the plate so that the work areas are comparatively smooth and level with the grain valleys. After etching, the plate is washed in alcohol to remove the etching solution and then is treated immediately with an ink-receptive lacquer which prevents oxidation of the fresh metal surface. The plate is then treated with a developing ink which is absorbed by the printing areas of the plate, after which the plate is washed with water to remove the light-hardened coating from the non-printing areas of the plate. The plate is now ready for use. The important properties of a deep-etch plate are roughness ratio, surface-void volume, and grain depth.[74] The depth of the etch is uniform and the size of the halftone dots varies, which is similar to the situation in relief printing, but opposite to that in gravure printing.

During printing, the plate is moistened with fountain solution or desensitizing solution containing ammonium dichromate, gum arabic, and phosphoric acid. The purpose of this dampening solution is to make the plate more receptive to water in the non-work areas and to prevent the adsorption of hydrophilic materials. The effectiveness of gum arabic as an etch is due to the presence of carboxylic groups, the number of which is increased by the chromic acid in the etch. Carboxymethylcellulose has proved to be a fair substitute for gum arabic. The solution must be acid, as in the case of albumen plates, because the adsorbed film of gum arabic on the plate surface is stable only in the acid region. Under favorable conditions, only a small amount of the dampening solution is needed, just enough to dampen

[74] G. A. H. Elton and G. Macdougall, *J. Soc. Chem. Ind. 65:* 212–215 (1946)

the plate and keep the non-printing areas clean. However, when printing with a poorly made plate or in times of carelessness, so much dampening solution may be used that trouble results from weakening of the image, poor drying of the ink, or excessive expansion of the paper.

Offset Printing

Originally, lithography involved printing from a stone or plate directly onto the paper. This is known as direct lithography. Very few stones are used today, but some direct printing is done from metal plates, notably for the printing of posters and cigar labels. Most lithography is done by offset in which a rubber-covered roll is used to transfer the printed design from the printing plate to the paper. The offset principle of printing was introduced in about 1906. An offset press consists of the plate cylinder, a system of inking rolls for applying ink, a system of fountain rolls for applying water, a rubber-covered offset roll which receives the image from the plate cylinder, and an impression cylinder to which the paper is attached and which presses the paper against the offset roll. A schematic drawing of an offset press is shown in Figure XIX-2.

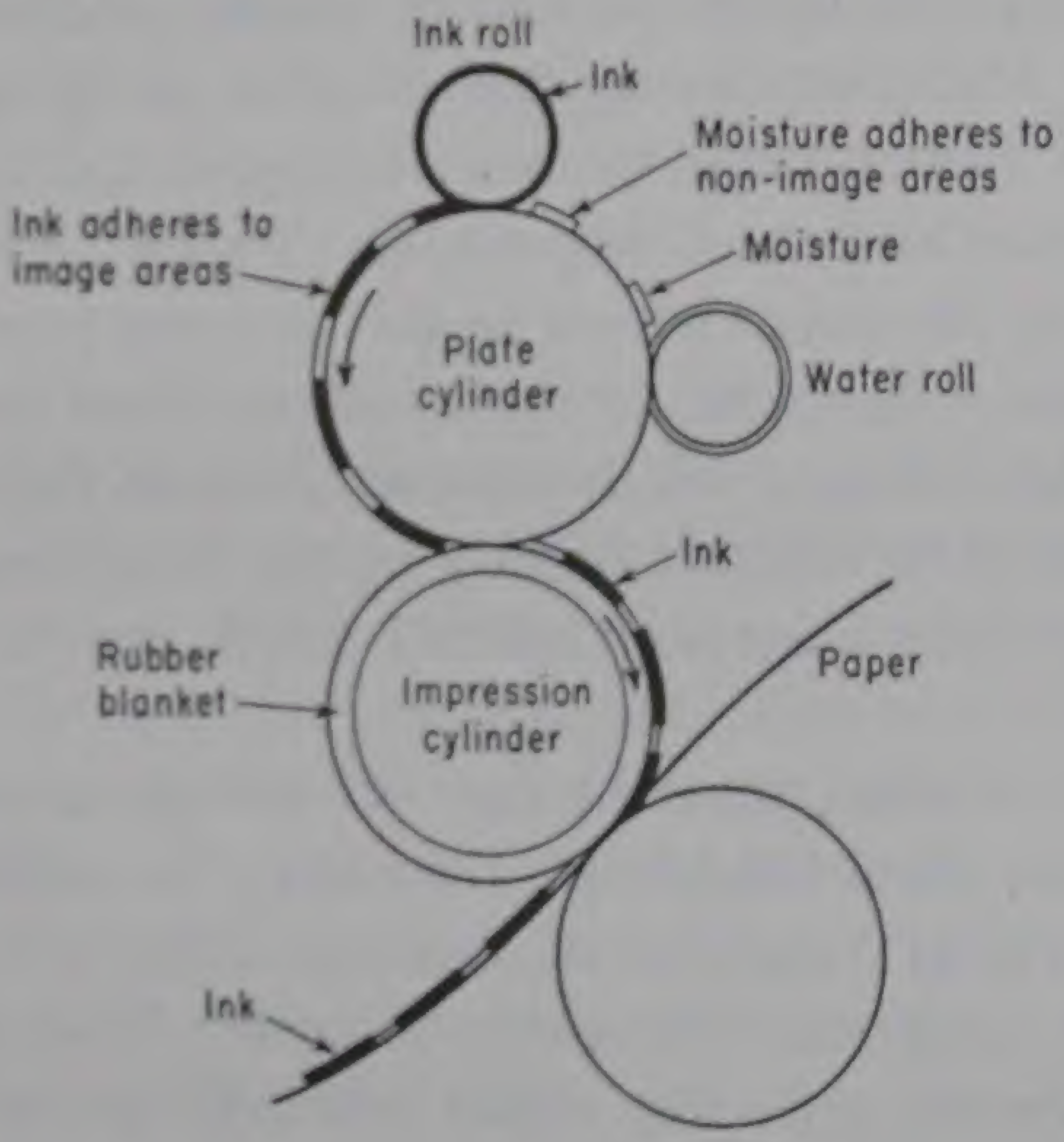

Fig. XIX-2. Diagram of the offset press principle.

The offset process has several advantages over relief printing in that (*1*) it uses less pressure, (*2*) it uses the original image plates, (*3*), it requires less time in makeready, (*4*) it consumes less ink, (*5*) it prints rough papers, and (*6*) the individual dots blend together in halftone printing to produce a print of soft, pleasing quality. Static electricity is less of a problem in offset than in relief printing because of the higher moisture content of the paper and the presence of moisture on the offset roll. As a rule, static is not a serious problem in offset unless the relative humidity of the pressroom atmosphere is less than 30%.

The offset process has the following disadvantages: (*1*) the plates are sensitive to mechanical abrasion and chemical attack; (*2*) the process requires a paper of high surface strength; (*3*) register troubles are frequent; (*4*) printing by offset requires a high degree of skill on the part of the pressman. Formerly offset printing lacked color intensity but this has been overcome by the development of strong inks. The prints are not as sharp as those from type, but good results are obtained. Very fine screens, up to 400 lines, have been printed by offset, and 150-line screens are in common use for fine detail halftones on coated papers. Process printing can be done by single impression presses or by two-, three-, four-, and six-color presses. Most offset presses print single sheets, although web presses are in use.

Planographic Inks

Planographic inks are very similar in properties to relief inks except that they are normally made in heavier body and color concentration. Heavier and more highly pigmented inks are required to prevent mixing of the ink and water on the press and to obtain satisfactory color values from the thin ink film normally applied in offset printing. If the concentration of pigment in the ink is too low, fading of the ink may result, although fugitive colors also cause this trouble. Fading of colored inks sometimes takes place in the tints and not in the mass color, and vice versa, although the permanent colors do not show fade in either strength. The type of extender used in making a tint has some effect on fading quality. As a rule, offset inks must be reduced slightly by the pressman just before use, but recently, offset inks have been offered which can be used just as received.

Ink for offset printing must be free of strongly alkaline materials or inorganic acids since these might etch the plate. In addition, alkaline materials tend to react with the acid in the fountain water to form water-soluble compounds which upset the ink-water balance. Water-soluble coloring matter should be absent, since this would mix with the water on the offset roll. Surface-active agents are undesirable if present in high concentration, since they tend to cause emulsification of ink in the water on the press. There is always some mixing of ink and water on an offset press, and after running for a considerable period of time, the ink may contain as much as 5 to 15% water. Water in the ink is not particularly harmful, although drying of the ink is appreciably retarded if there is much over 5 to 7% water in the ink. It is important, however, to prevent an ink-in-water emulsion from forming, since this results in a condition known as "washing" in which a light film of ink is printed where it should not be. Free fatty acid in the ink may cause trouble by becoming adsorbed on the grained surface of a defective plate, causing the plate to pick up ink in the non-work areas.

Many offset inks contain no driers. A great many ink makers do not add drier to their inks, since inks lose drier in storage, but many ink makers add drier and count on loss of drier in storage. Many pigments are natural driers and when added to inks, driers are not required. As a rule, offset inks tend to dry more slowly than relief inks, although this is capable of adjustment by the pressman. In cases of slow drying, it may be necessary to spray the printed sheets with a slurry of talc, gum arabic, or starch to prevent offset.

General Requirements of Paper for Offset Printing

The planographic process is widely used for the printing of paper labels, children's books with colored illustrations, posters, billboards, bank checks, and more recently, for the regular printing of books. There are some advantages to printing newsprint by offset,[75] and several fairly large newspapers are printed this way. Some of the common grades printed by the planographic process are uncoated offset book (ranging in basis weight from 50 to 100 lb., 25 × 38—500), coated offset book (ranging in basis weight from 60 to 100 lb., 25 × 38—500), uncoated lithograph (ranging in basis weight from 45 to 70 lb., 25 × 38—500), coated lithograph (usually 60 lb., 25 × 38—500), litho blanks (coated book-lined card middles), litho box wrap (coated one side), and litho coated labels (coated one side).

Smoothness. In the early days of lithography when printing was done directly from stone or metal plates, it was necessary to use smooth-surfaced papers in order to obtain good reproduction of fine prints. However, with the invention of the offset process, in which a flexible rubber blanket is used to transfer the ink from the printing plate to the paper, it became possible to print fine halftones on rough-surfaced papers. As a consequence, paper for offset printing need not have a smooth surface like that required for relief printing. Fine halftones can be printed satisfactorily on uncoated offset book papers having finishes ranging from antique and eggshell to machine and English finish. In fact, in the early days of offset printing a certain amount of grain or tooth was considered essential to permit entrapped air to leak out, but this is no longer considered necessary.

Ink Receptivity. Paper for offset must have good ink receptivity in order to permit the uniform removal of ink from the offset blanket, since otherwise the ink will pile on the plate and blanket, causing fill-up of fine halftones. The paper must have a fair degree of absorbency in order to prevent squashing of the ink film between the offset blanket and the paper.

Chemical Requirements of Offset Papers. There must be no gritty or abrasive particles in offset papers, since these might come loose from the paper and scratch the plate surface, producing a condition known as scumming where the ink is attracted to the non-work areas. The presence in the paper of excess water-soluble chemicals (e.g., free alkali, acids, alum, or chlorides) also causes scumming by chemically attacking the plate. The paper must be free of surface-active agents since these tend to leach out in the dampening solution and cause emulsification of the ink.

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[75] C. F. Geese, *A. N. P. A. Mech. Bull.* No. 323: 141-144 (Sept. 9, 1946)

Offset paper must not be too alkaline, since alkalies tend to neutralize the acid in the fountain water, making it necessary to raise the *p*H of the water, possibly to the point where trouble occurs. Most uncoated offset papers have a *p*H around 5.0, and consequently do not cause trouble. Coated papers containing alkaline pigments are the most frequent cause for complaint.

Surface Bonding Strength. Because of the thin ink films and stiff inks used in offset printing, picking is more of a problem than it is in relief printing. Thus, in order to print satisfactorily by offset, it is necessary to have a stronger paper surface than that used for relief printing.

The surface of offset papers should be free of loose fibers, and the surface fibers should be firmly bonded to the body of the paper. In the printer's terminology, the paper should be hard and tight. Soft papers (e.g., newsprint) cannot be printed satisfactorily by offset because of linting. The stock for making offset papers is generally beaten more than the stock for regular book papers.

Offset papers are usually surface-sized with starch to strengthen the surface of the paper and prevent lintiness, thus producing a hard surface over a relatively soft, resilient base stock. It is necessary, however, that the body of the paper be strong enough to resist splitting on the press. Trouble will occur if the surface of the paper is very hard and oil-resistant, while the interior of the paper is soft, because the ink will have to be so tacky to take on the resistant paper surface that the pull of the ink on the paper causes an internal rupture of the paper. The Government Printing Office specifications for uncoated offset require that the paper pass a No. 11 Dennison wax on both sides. It is possible, however, for offset papers to be surface-sized to the extent that they pass a No. 14 Dennison wax and yet undergo body stock splitting when printed, because of the low internal strength of the paper. The remedy in this case is to adjust the surface sizing to obtain a greater penetration of size into the interior of the paper. Paper for gelatin-plate printing must have a pick test better than Dennison wax No. 22.

Moisture Control with Offset Papers. Proper moisture control is a highly important consideration in offset printing. Lack of proper moisture control results in curl and dimensional instability of the paper on the press, causing distortion of the printing image and improper positioning of the paper. Misregister can result from bad press conditions, as well as from faulty paper, but most cases of misregister on successive printing on an offset press can be traced to distortion of the paper. A change in the dimensions of 1/50 of 1% during printing is enough to cause trouble.[76]

It is well known that paper is hygroscopic and changes in dimensions with changes in moisture content. Paper expands less in the machine direction than in the cross direction, and for this reason, printing papers for sheet-fed presses are usually cut with the grain or machine direction the long way of the sheet in order to keep the stretch and shrinkage on the shortest dimension (i.e., the cross direction). The sheets are fed to the press with the machine direction parallel to the axis of the press roll; this is done because the pressman can compensate for expansion and contraction around the roll (by changing the packing), but he cannot make adjustments for dimensional change in a direction parallel to the roll axis. Also the sheet lies against the cylinder better when fed in this fashion. Brown[76a] found, however, that the resistance to picking in the case of machine-coated paperboard was less when the sheets were fed with the grain around the printing cylinder. However, paper is usually fed grain parallel to the roll axis and consequently the misregister taking place during printing is directly related to the coefficient of linear expansion in the machine direction. Weber[76] suggests a high ratio of machine direction to cross direction folding endurance as a measure of the most desirable formation for close register in printing. Seasoned paper prints better than green or freshly made paper because of its greater stability.

Dimensional changes in paper are almost directly proportional to changes in the moisture content,[77] and hence it is necessary to stabilize the moisture content of paper if trouble-free printing is to be obtained. The relation which exists between the moisture content of the paper and the humidity of the pressroom atmosphere is of great interest to the lithographer. Paper shows less dimensional change between relative humidities of 40 to 60% (corresponding to a moisture content between 5 to 7%[78]) than at higher or lower humidities, greatest stability being obtained at about 45% R.H. A variation of 5% or less in the relative humidity of the atmosphere will cause faulty register.[79] Lithographers are aware of the importance of proper conditioning of paper, and it has long been the custom among lithographers to hang paper in the pressroom until it comes to equilibrium with the plant atmosphere. In some cases, the pressroom is air-conditioned to prevent fluctuations in relative humidity.

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[76] C. G. Weber, *Paper Trade J. 109*, No. 16: 205–209 (Oct. 19, 1939)

[76a] B. F. Brown, *Paper Mill News 73*, No. 28: 54–56 (July 15, 1950)

[77] R. F. Reed, *Paper Trade J. 107*, No. 4: 25–28 (July 28, 1938)

[78] H. O. Ehrisman, *Paper Trade J. 103*, No. 1: 1–4 (July 2, 1936)

[79] "Air Conditioning in Printing and Lithographic Plants," Parks-Cramer Company Bulletin No. 1029, through W. Dahl, *Paper Trade J.*, pp. 329–332 (June 29, 1939)

The problem of dimensional stability is not so great in relief printing as it is in offset printing. If paper for relief printing is conditioned so that its moisture content is in equilibrium with the atmosphere, there will be no change in dimensions during printing with ordinary inks. However, if heat is used to set the ink, the moisture content of the paper may be reduced to 3.2 to 3.5% during drying,[80] which is enough to change the dimensions and affect the strength of the paper.

In offset printing, it is not enough to condition the paper before printing, inasmuch as during printing, water is transferred to the paper by the dampening solution. Part of this water evaporates, but even if the printer operates his press with a minimum amount of dampening solution, enough water will be transferred to the paper to cause a dimensional change. In multicolor offset, a complete printing may comprise up to twenty trips through the press, which gives an idea of the opportunities for absorption of water by the paper. A 60-lb. offset paper can easily pick up 1% moisture in printing four colors.[81] This is sufficient in the case of a sheet 40 × 54 in. to result in an expansion of 1/64 in. in the machine direction and 3/64 in. in the cross direction, enough to cause misregister.

Paper which is conditioned to equilibrium with the pressroom may pick up an additional 0.5 to 1.0% moisture on the offset press and still be in equilibrium with the atmosphere after printing.[82] This is due to the hysteresis effect by which paper readjusts itself in moisture within its hysteresis limits from the lower (absorption) to the upper (desorption) curve. Hysteresis is a factor in offset printing because much commercial paper is dried on the paper machine to a moisture content which is lower than that which corresponds to the equilibrium moisture content of the paper under pressroom conditions. For example, paper is commonly dried on the paper machine to a moisture content of 3 to 5%, whereas its equilibrium moisture content under pressroom conditions is usually 6 to 8%. Thus, when the paper is conditioned before printing, it approaches its equilibrium moisture content from the low side (i.e., the absorption of moisture), and consequently can pick up additional moisture during printing and still remain within the hysteresis limits. If such a paper is used in multicolor printing, it will show a progressive increase in moisture content for the first five to six printings, even if the paper is brought back to equilibrium with the pressroom after each trip through the press.

[80] C. MacArthur, *Paper Trade J. 105*, No. 15: 219–220 (Oct. 7, 1937)

[81] R. F. Reed, *Paper Trade J. 130*, No. 12: 31–36 (Mar. 23, 1950)

[82] C. G. Weber and M. N. Geib, *Paper Trade J. 103*, No. 12: 210–214 (Sept. 17, 1936)

It is possible to precondition paper before printing at a humidity higher than that existing in the pressroom and then condition at the same humidity existing in the pressroom so that the paper approaches equilibrium from the high side, i.e., by the desorption of moisture. Such a paper can be printed with no permanent gain in moisture content, since it is already at its maximum moisture content within its hysteresis limits.[83] This does not mean that the paper cannot pick up moisture during printing; it simply means that the sheet can be reconditioned before each passage through the press so that it can be started through the press with the same starting moisture content, and the change in moisture content will be the same each time.

The best solution to the moisture problem in offset printing is to adjust the moisture content of the paper before printing so that it loses moisture to the atmosphere at the same rate that it absorbs moisture from the press, thus preserving the proper moisture balance throughout the run. In order to obtain this result, the moisture content of the paper at the start of the run should be about 0.5 to 1.0% higher than it would be if the paper were in equilibrium with the pressroom atmosphere. Recent bulletins of the Lithographic Technical Foundation recommend that offset paper should contain, at the time of printing, between 5.5 to 5.8% moisture when used in air-conditioned pressrooms at 45% relative humidity, and between 6.0 to 6.5% moisture when used at a relative humidity of 50%, but these values depend somewhat on the grade of paper. This corresponds to conditioning of the paper at a relative humidity of 5 to 8% above that of the pressroom.[84]

The ideal situation is for the printer to buy from the manufacturer preconditioned paper which has been wrapped in a moisture-vaporproof wrapper,[85] and then use this paper in an air-conditioned pressroom. If it is impractical to buy preconditioned paper, the printer can condition the paper himself by storing at a relative humidity of about 5 to 8% above the relative humidity of the pressroom. The value of proper preconditioning is illustrated in Figure XIX-3,[86] where the pick-up of moisture during a nine-color press run is shown for (*a*) an unconditioned paper, (*b*) a paper conditioned at pressroom humidity (45%), (*c*) a paper conditioned at a relative humidity 8% above that of the pressroom (53%), and (*d*) a paper conditioned at a much higher humidity (65%) and then reconditioned at 8% above that of the pressroom (53%). The unconditioned paper picked up 0.9% moisture during the press run and consequently changed appreciably in dimensions. The sheet conditioned at pressroom conditions (45% relative humidity) picked up 0.6% moisture and also changed dimensions appreciably. On the other hand, the sheet conditioned at a relative humidity 8% above that of the pressroom (a humidity of 53%) remained constant in moisture content during printing. The fourth sample, which had been conditioned at 65% relative humidity and then conditioned again at 53%, also picked up no moisture during printing, although it had a higher initial moisture content, as would be expected from the hysteresis effect. The effect of preconditioning on the amount of misregister obtained during a seven-color press run is shown in Table IV, where it can be seen that the best register is obtained with paper having a moisture content about 0.5% above that corresponding to equilibrium.[87]

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[83] R. F. Reed, *Paper Trade J. 107*, No. 4: 25–28 (July 28, 1938)

[84] C. G. Weber and M. N. Geib, *Paper Trade J. 103*, No. 12: 210–214 (Sept. 17, 1936)

[85] H. R. Russell, *Paper Mill News 73*, No. 22: 11, 14 (June 3, 1950)

[86] R. F. Reed, *The American Pulp & Paper Association Superintendent's Yearbook*, 1948, pp. 210–216 "(through courtesy of Lithographic Technical Foundation)"

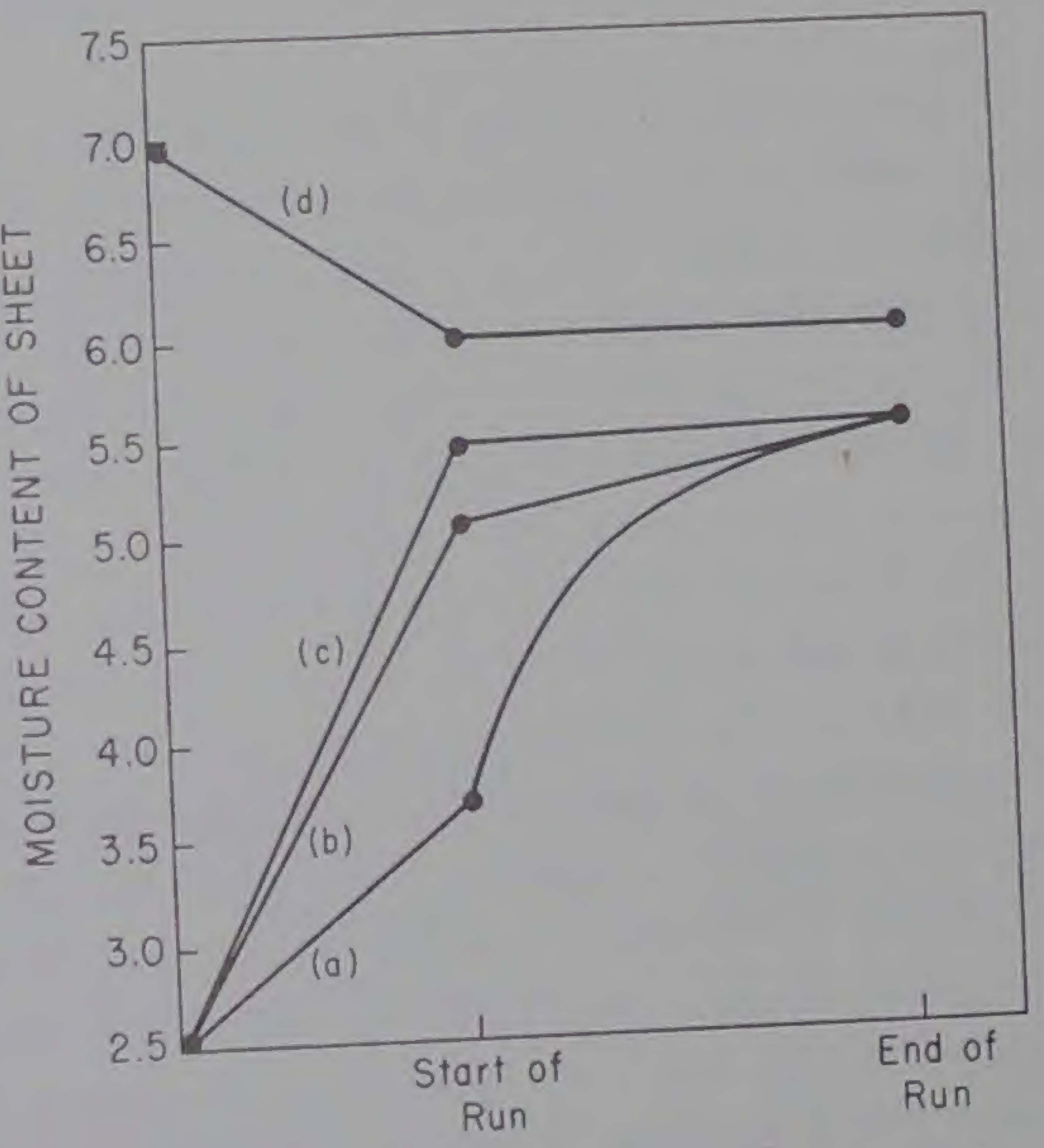

Fig. XIX-3. Effect of conditioning of paper on the moisture content during a nine-color press run (offset).[86] (a) Not conditioned; (b) conditioned at pressroom humidity (45%); (c) conditioned at 8% above pressroom humidity (53%); and (d) conditioned at 65% relative humidity and then at 53%.

Preconditioned paper purchased in moisture-vaporproof wrappers should not be taken from the wrapper until temperature equilibrium has been reached. If the unwrapped paper is cooler than the atmosphere, it will cool the surrounding air, with the result that the edges of the paper take on more moisture and become wavy.[88] If the paper is at a higher temperature than the atmosphere, the opposite effect is obtained, namely, the edges become tight. The temperature of the pressroom air should be maintained constant (as well as the humidity), because paper changes in temperature more slowly than air. A rise in pressroom temperature in plants with automatic humidity control means that more moisture will be added to the air, and since the paper tends to cool the air close to it, the paper will pick up additional moisture, thus causing wavy edges. When the temperature of the pressroom is decreased, the opposite occurs and the pile of paper develops tight edges. Wavy edges can sometimes be corrected in the print shop by exposing a pile of the wavy paper to infrared lamps to dry out the edges of the paper.

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[87] C. G. Weber, *Paper Trade J. 109*, No. 16: 205–209 (Oct. 19, 1939)

[88] R. F. Reed, *Paper Ind. 28*, No. 12: 1741–1743 (Mar., 1947)

TABLE IV

RELATION OF PAPER CONDITIONING TO REGISTER IN OFFSET PRINTING

Paper number	Approximate moisture content,[a] %	Average misregister in 7-color press run,[b] in.
1	0	−0.023
2	+2	+0.024
3	−2	−0.093
4	+0.5	±0.002

[a] Moisture content measured above or below that corresponding to equilibrium in the pressroom.

[b] Plus values refer to the number of inches outside of first color, whereas minus values refer to the number of inches inside of first color.

Roll paper for web offset does not present as serious register problems as sheet paper. Roll paper should be slightly on the dry side in order to reduce shrinking of the exposed edges and to reduce edge cracks and web breaks.[89]

Curl in Offset Papers. Special care must be taken in the manufacture of offset papers to prevent waviness or curl, since curl causes trouble by interfering with the action of the feeder mechanism and register guides, thereby causing the sheet to feed unevenly and affecting the register. A higher degree of flatness is required in offset papers than in papers for the relief process, because the 100% impression in offset causes buckling or fanning out if the paper is not entirely flat. Fanning occurs at the edge of the sheet away from the grippers where the paper is not held securely.

Curl may be inherent or built-in curl, or it may be caused by uneven expansion or contraction of the paper due to changes in moisture content. Too much moisture on the plate in offset printing will cause curl. Curl is worse with thin, hard papers than it is with bulky, soft papers, and is greatest during periods of low humidity. It is a serious problem when printing papers treated on one side only, e.g., gummed labels. The subjects of dimensional stability and curl are discussed further in the chapter on the properties of paper.

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[89] R. F. Reed, *Paper Trade J. 130*, No. 12: 36–38 (Mar. 23, 1950)

Coated Papers for Offset Printing

Within recent years, the printing of coated papers by offset has increased,[90] and now considerable offset printing is done on coated stock. Coated papers are preferred for four-color process printing by offset. Brilliant effects are obtained on coated papers, since the coating tends to keep ink on the surface of the paper where it has a greater brilliance. On the other hand, coated papers have lower strength, poorer folding qualities, and lower water resistance than uncoated papers, and consequently are not desirable for all offset printing. Furthermore, offset printing on coated stocks frequently produces a slurred impression caused by a slight slipping of the rubber blanket resulting from excessive ink and excessive pressure used in the areas of heavy lettering or halftone shadows.[91] Printing on uncoated paper results in a softer appearing print than that obtained on coated paper because of the grain of the paper, and because the offset dot is not so sharply outlined. This softness is desirable on certain multicolor printing jobs.

Printing of coated paper by offset presents certain difficulties which are not so critical in relief and gravure printing. Coated papers for offset must be stronger than the corresponding papers for relief printing in order to withstand the 100% impression of the offset roll and to resist the greater pull exerted by the thinner, more viscous ink films used.[92] Coated papers for offset should pass a Dennison wax of 6 or 7 (compared with about 4 or 5 for relief printing). The high strength required in offset papers means that high percentages of binder must be used in the coating, and this tends to slow down the drying of the ink. The drying problem is further aggravated by the fact that the ink often contains moisture picked up on the press.

In addition to the moisture transferred to the paper in emulsified form in the ink, additional moisture is picked up by the paper directly from the offset roll. In certain coated papers, this moisture causes softening and loosening of the coating. The loosened coating tends to work its way into the ink where it attracts water to the ink, increasing the viscosity and causing piling.[93] The loosened coating also acts as an abrasive on the plate, causing it to scum, i.e., accept ink in the non-printing areas. Coated papers containing casein as the adhesive are less susceptible to these troubles than coated papers containing starch as the adhesive, and consequently, casein-coated papers are preferred for offset printing. Starch-coated papers can be printed by offset, but care is necessary in printing. On the other hand, casein-coated papers are likely to contain water-soluble substances which

[90] R. F. Reed, *Paper Trade J. 102*, No. 22: 281–283 (May, 28, 1936)

[91] M. H. Bruno, *Paper Trade J. 130*, No. 24: 98, 100, 102 (June 15, 1950)

[92] R. P. Long, *Modern Lithography 10*, No. 9: 24–28 (Sept., 1942)

[93] M. Zucher, *Tappi 32*, No. 9: 398–399 (Sept., 1949)

work into the ink and cause emulsification of water in the ink. If too highly waterproofed, casein-coated papers may be so non-receptive that moisture accumulates on the blanket and works its way into the ink. This latter trouble accurs most often on multicolor presses where the second color is applied before the moisture added in the first impression has had a chance to be absorbed.

A *p*H of 8.0 for the coating layer is about optimum from the standpoint of ink drying. A neutral or slightly acid coating tends to retard drying,[94] as illustrated in Figure XIX-4, which shows the relationship between the *p*H of the coating, the relative humidity of the atmosphere, and the drying time of the ink. On the other hand, a highly alkaline coating tends to lower the *p*H of the fountain solution. A *p*H of 6.0 to 7.0 for the coating layer is usually obtained when clay is used as the pigment, and this is generally satisfactory. Coated paper containing calcium carbonate as one of the pigments often causes trouble because of the sensitivity of the carbonate to the acid in the fountain water. Some calcium carbonate can be used, however, if the coating is sufficiently water-insoluble. Lithopone has been known to cause trouble in coated offset papers by reacting with the acid in the fountain water to liberate hydrogen sulfide, which combines with lead in the printing ink to cause a blackening of the ink. Coated papers containing

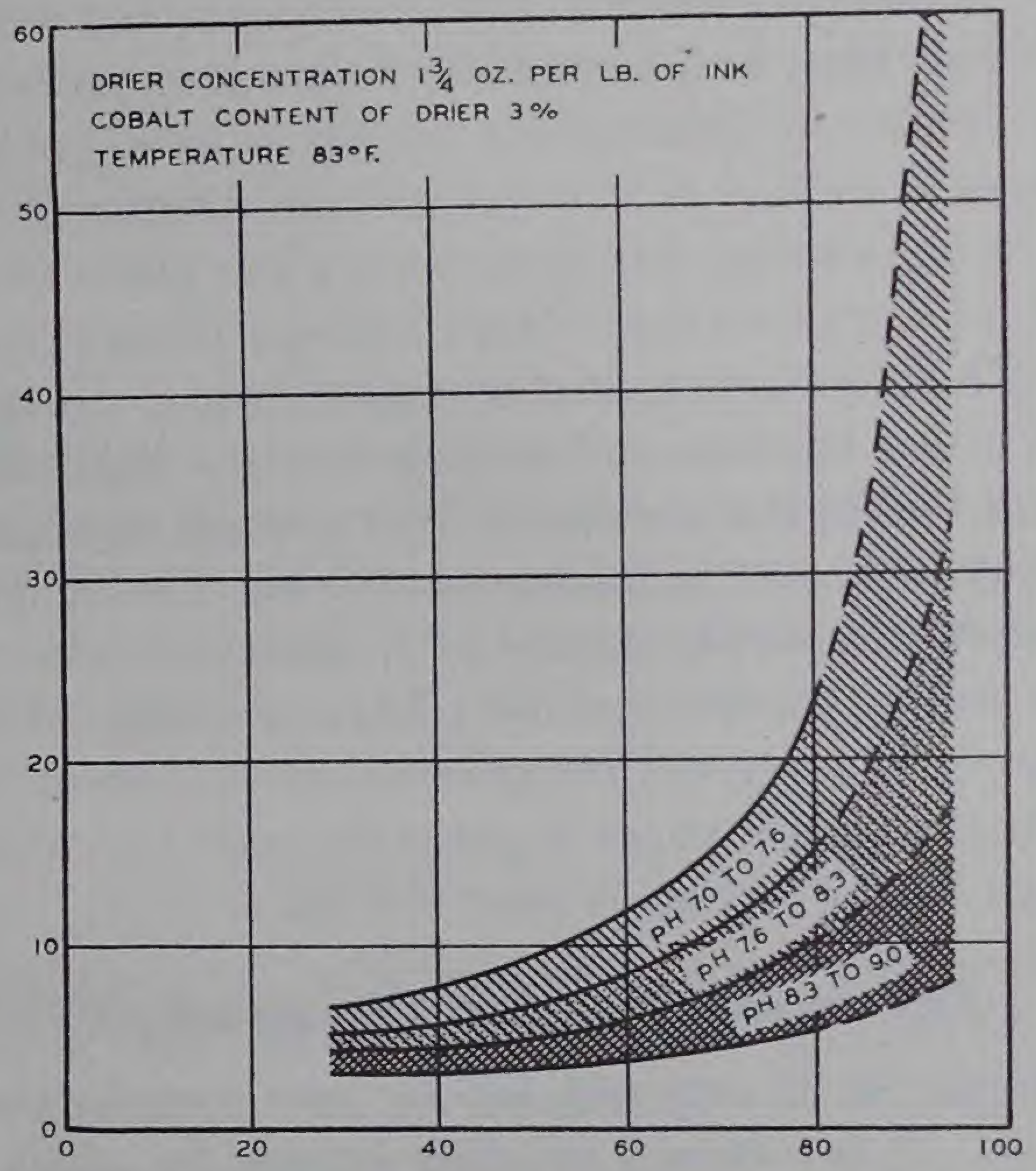

Fig. XIX-4. Effect of *p*H of coated paper and relative humidity of atmosphere on the drying time of offset ink.[86] Abscissa, relative humidity in per cent; ordinate, drying time in hours.

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[94] R. F. Reed, *Paper Trade J. 120,* No. 25: 76–80 (June 21, 1945)

satin white usually cause trouble and are rarely used for offset printing. The presence of surface-active agents in coated papers sometimes causes trouble by lowering the surface tension of the water on the plate to the point where ink will emulsify in the water.

Photogelatin (Collotype) Printing

Photogelatin printing, sometimes known as collotype, albertype, or phototype, is a planographic printing process similar to lithography, which is used for short runs (100–4,000 copies) when special effects are desired, for example, for postcards, posters, special displays, and art work. Collotype printing differs from ordinary planographic printing in that no screen is used. This results in illustrations having a true gradation in tone; hence, the process is known as continuous tone printing.

Early collotype printing was done with glass plates having a bichromate sensitized albumen coating. More modern printers use special aluminum plates. The plate is prepared by exposing to a strong light through a film negative which hardens and waterproofs the light-sensitive coating on the plate according to the amount of light passing through the negative. The plate may then be heated to further harden the albumen image. During printing, the plate is alternately treated with water and ink. The degree of hardness of the coating determines the relative amounts of ink and water picked up by the plate, which in turn governs the amount of ink transferred to the paper. English finish paper is generally used for collotype printing. The paper should pass a Dennison wax No. 22.

Silk-Screen Printing (Serigraphy)

Silk-screen printing is very old, having been used by the early Egyptians and Chinese. It is a stencil printing process by which ink is forced through a stencil mounted on a silk screen stretched tightly over a frame. A rubber blade is used to force the ink through the stencil onto the surface of the paper. Stencils may be cut by hand or they may be photographed or painted on the screen. If photographic means are used, a sensitized coating must first be applied to the silk screen.

Silk-screen printing is used mostly for special effects, e.g., for display cards, lamp shades, and special wallpapers. The process is used for short runs, and only for the printing of illustrations. Much silk-screen printing is done by hand. One particular advantage of the process is that objects of practically any shape can be printed.

Pressroom Difficulties

Difficulties in the pressroom may arise from faulty ink, faulty paper, or unfavorable pressroom conditions such as poor ink distribution or faulty rollers. Either the ink, the paper, or the press may be wholly responsible for the trouble, or the trouble may be caused by a combination of factors. For example, lack of detail in the fine work may be caused by a faulty or worn plate, soft or improper makeready, lack of smoothness in the paper, or an ink which is too short or too soupy. On the other hand, certain troubles may be fairly definitely related to a specific condition as, for example, ghosting, a very light repeat of form showing up in solid areas, which is generally caused by faulty distribution of ink resulting from deformed rollers.

In analyzing printing troubles, it is helpful to look for patterns which will give a clue to the cause of the trouble. If the trouble occurs at the same location in successive sheets, rather than at random over the surface of the paper, the chances are that it is due to faulty press adjustment. If the trouble occurs more or less regularly on every second, third, or fourth sheet, it is likely that the paper was sheeted at the paper mill either two, three, or four rolls at a time, and that one of the rolls of paper was inferior. A gradual fading or darkening of color in a particular direction on the printed sheets is an indication of faulty ink distribution.

Printing problems have increased greatly in recent years because of the increased complexity of printing presses, the increase in multicolor printing, and the speeding up of printing presses. Some of the common printing troubles and their remedies are discussed in the following sections.

Strike Through

Strike through is the staining of the reverse side of the printed paper by oil vehicle or ink which has penetrated through the paper. Strike through may be caused by an ink, a paper, or a press condition. If the ink vehicle is too low in viscosity or if the pigment in the ink is poorly dispersed, strike through may result. If the paper is too absorbent, strike through will result. Too much impression on the press in relief printing will tend to force the ink into the paper and cause strike through.

Strike through may be corrected by changing to a heavier bodied ink or to a faster drying ink, or by using less ink on the press. Sometimes the addition of magnesia or talc to the ink will help. Changing to a paper of lower porosity also helps.

Sometimes it appears that the ink has penetrated completely through the paper, whereas what actually has happened is that the oily vehicle has separated from the ink and penetrated beyond the pigment. This lowers the opacity of the paper and makes the ink visible on the back of the sheet. In cases where this situation has occurred, it is possible to measure the relative penetration of ink and vehicle into the paper by progressively peeling off layers of the printed paper, by using Scotch tape. If this is done under a binocular microscope, the point beyond which no ink particles have penetrated can be readily detected. The distance of penetration can be measured by checking the caliper of the paper before and after the various layers have been peeled off with the Scotch tape.

Show Through

Show through is the visibility of printing on the reverse side of the paper. It may be caused by paper which is too low in opacity, or by paper which is poorly formed; or, as explained above, show through may be caused by excessive penetration of ink vehicle into the paper, causing a reduction in the opacity of the paper. Show through is basically a paper problem, although using less ink on the press will sometimes help the situation. The real remedy for show through is to increase the opacity of the paper and to improve the formation.

Offset

Offset is the unintentional transfer of wet ink from the printed paper to the back of the following sheet, due to top tack on the surface of the ink film. Offset is more prevalent in halftone printing than in solids and ordinarily is more prevalent in offset printing than in relief printing. Offset is very common when non-drying inks (e.g., news inks) are used and when overprinting one color on another. Offset is very serious when thick ink films are applied, as when forcing halftones.

Offset results when the oil absorption of the paper is too low. Other conditions causing offset are: too much moisture in the ink (in lithographic inks), poor fountain adjustment, too much ink necessitated by improper makeready, too much ink necessitated by lack of color strength in the ink, rollers set too heavily on the form causing ink to collect at the ends of the plate, too much impression, too much static causing the printed sheets to draw closely together and attracting ink from one surface to the other, poor delivery of the printed sheets, forced production, and rough handling of the printed paper. Offset occurring in the smashing of printed matter for books is due to poor drying of the ink. Offset is basically an ink and press problem, rather than a paper problem. Most papers can be printed without offset if the proper ink and proper press conditions are used.

Increasing the rate of drying of the ink by using heat-set and vapor-set inks has helped in overcoming offset. Using a stronger ink and running less ink on the press will generally help in preventing offset. Offset may be overcome by incorporating waxy or oily offset compounds in the ink which tend to exude to the surface of the ink film during drying; usually, about ½ to 1 oz. of offset compound per pound of ink is used. Spraying starch or gum arabic on the printed paper helps to prevent offset. The starch or gum may be sprayed either in dry form or after suspending in water, but must be used uncooked so that the starch or gum particles lie on the surface of the printed sheets where they hold the sheets apart and prevent contact of the wet ink film with the back of the next sheet. Either potato starch or a special grade of corn starch is used. Another remedy is to resort to slip sheeting, by which a blank or waste sheet of paper is inserted between the printed sheets to protect the wet printed surface from offsetting on the back of the next printed sheet. Slip sheeting is too expensive to use on most printing, but it is sometimes used on especially fine printing jobs. Use of a bottomless box at delivery will assist in preventing offset.

Collecting

Collecting is a condition resulting from the collection of foreign matter on the press plate. This matter may be loose fuzz from the surface of the paper, excessive trimming dust from the paper, or pigment removed from coated or heavily loaded paper. Such foreign matter tends to transfer to the printing plate during inking, thus leading to an impression composed of a small dot surrounded by a white ring. In extreme cases, collecting may make it necessary to shut down the press and wash up.

Collecting may be caused by paper which is insufficiently sized with rosin or starch, by too tacky an ink, or, in the case of offset printing, by a tacky offset blanket. Collecting occurs most frequently when printing the wire side of the paper because of the greater number of loose fibers (whiskers) on this side.

The remedy for collecting is to avoid loose fuzz or dust on the paper by brushing the edges of the piled paper before printing. Fuzz and dirt on the press and in the atmosphere should be held to a minimum. If the ink is too tacky, a wax-reducing compound may be helpful. Collecting is often taken care of by using a tacky first form roller, which will pick up any specks and move them back into the ink system or cover them up on the printing roller so that the specks will not repeat.

Caking or Fill-up

Caking or fill-up is the tendency toward a filling up of the fine work on a halftone plate. Anything which prevents the proper removal of ink from the printing plate will cause caking or fill-up. One cause is improper dispersion of pigment in the ink vehicle. Insufficient vehicle in the ink will also cause fill-up, as will an ink which is too heavy or too soft.

The remedy for fill-up is to clean the press and then change the ink. If the ink is too thin, heavy varnish may be added. If the ink is too heavy, the addition of a reducing varnish, a No. 0 or No. 1, may help. In some cases, it may be necessary to regrind the ink. Running less ink on the press is sometimes beneficial.

Piling

Piling is the uneven collection of ink on the press plate, rollers, or, in the case of offset printing, collection on the rubber offset blanket. Piling is closely related to fill-up. It may be caused by ink which is too short or by paper which has too low an ink receptivity. In offset printing, piling may be caused by the emulsification of a large amount of water in the ink, causing the ink to become putty-like in consistency.

When piling occurs in offset printing as a result of emulsification of water in the ink, the addition of a heavy varnish may help by causing the ink to repel the water more effectively. Another remedy is to change to a new ink of longer body and better receptivity for the paper. Too much drier in the ink will sometimes cause piling.

Crystallization

Crystallization results in the poor bonding of top colors to the base or first-down colors, for example, poor bonding of a red to the first-down yellow when producing an orange. When crystallization occurs, the last-down colors are easily rubbed off the base color.

Crystallization may be due to the presence of too much drier in the first-down color which causes it to dry out before the second color is printed. Lack of penetration of the first-down color into the paper may also be a factor.

One remedy for preventing crystallization is to retard the drying of the base color by the addition of oily or waxy materials. If the base ink has already crystallized, the second ink may be modified with a wax (beeswax) or similar material which causes it to take on the crystallized surface. Use of a thinner varnish or the addition of more drier to the later colors is often helpful.

Mottling

Mottling is unintentional irregularity or unevenness of the printed matter. There are a number of causes of mottle.

Mottling in the gray areas of halftones results from fill-up of the small spaces between the halftone dots causing irregular printing of ink from these spaces. This type of mottle can be controlled by using a minimum amount of ink.

Mottling in solid areas is generally caused by an ink which is too soft (an ink with too weak cohesive forces), or by an ink which has too much body. Too soft an ink gives a smeary mottle, whereas an ink with too much body gives a dry-looking mottle. Mottle in the solid areas of the printing may also be caused by the uneven absorption of ink by the paper, due to variations in ink receptivity of the paper. Too much ink on the plate, uneven distribution of ink (due to inferior ink or improperly set rollers), and too much or too little pressure during printing are other causes of spotty or mottled printing. Mottling caused by too soft an ink can be corrected by building up the body of the ink by adding No. 5 varnish or by mixing with another heavy-bodied ink. Improving the wetting of the pigment or the addition of talc to the ink is beneficial if the ink is too greasy. Using less ink is sometimes helpful.

Misregister

Misregister is a condition whereby the printing does not fall in the proper place on the paper. It may be caused by a faulty press adjustment or by paper which is not suited to the operation. It is fairly common on papers with wavy or feather edges, or on papers which have uneven edges because of poor trimming. Pick-up of moisture by paper during offset printing will cause misregister, due to expansion if the paper is not properly conditioned ahead of time. Misregister is difficult to overcome in the offset process because the printing plate is a single sheet of metal, and therefore it is not possible to shift plates as in relief printing, which means that the responsibility for good register lies chiefly with the paper. The special precautions necessary in preventing misregister in offset printing have already been discussed.

Misfit is a special type of misregister in which some images coincide and others do not. It is caused by uneven expansion or contraction of the paper.

Chalking or Powdering

Chalking is a condition in which the pigment in the dried ink film tends to dust or powder, thus producing a dull surface. Chalking is caused by too much absorption of vehicle and varnish into the paper, leaving the pigment in the ink without sufficient binder. The main cause of chalking is too low a viscosity of the vehicle. However, chalking also results if the drying of the ink is too slow, since this means that the varnish continues to penetrate until eventually too little is left with the pigment. Paper which has too low a moisture content is likely to cause chalking. The trouble occurs most frequently with heavily filled and coated papers, particularly where the coating is highly absorbent.

To overcome chalking, a hard-drying varnish (e.g., Overprint A—No. 1) may be added to the ink, or a heavier bodied ink may be used. The addition of more drier to the ink is sometimes helpful because it reduces the time in which the vehicle remains in a liquid state. In the case of coated papers, changing to a paper which has a stronger, harder sized coating will reduce chalking. In offset printing, a size or tint base may be printed on the paper to help prevent chalking.

Rubbing or smudging of the printed sheet during trimming and handling is a trouble related to chalking. The basic cause of this trouble is the same as that for chalking, i.e., insufficient binder in the ink film. The remedies are the same as given above. A wet ink film will also cause smudging.

Picking

Picking is a lifting of the surface of the paper by the ink. Picking is a common trouble which occurs mostly with coated papers, although it also occurs at times on uncoated papers. Generally, picking shows up as a white spot on the inked background, the white spot being where the ink has lifted some of the paper surface. White spots do not always indicate picking, however, since similar spots may be caused by bits of paper which have become stuck in the wet ink, or by spots which did not receive ink because of a damaged printing block. In some cases, the surface of the paper is not pulled loose, but is simply raised in the form of a blister. Picking is very undesirable, since it not only detracts from the printing in the place where the paper has been picked, but the particles lifted from the paper tend to lodge on the printing plate or be carried into the ink system. Picking is especially noticeable in solid printing areas.

Picking is predominantly a paper and ink problem. It may be caused by the ink drying too fast, by an ink which is too tacky, or by a weak paper or weak coating on the paper. Inks which have very high tack are likely to pick all but the most tightly bound paper surfaces (see relief printing inks). In multicolor printing, where one ink is printed over another while still wet (trapping), there is likely to be picking after the second or third impression, due to the weakening of the paper by the first impression; or if the first-down colors set too fast, picking may result as the second or third colors are printed. In order to avoid these difficulties, softer and softer inks are used in each succeeding printing. Too low a temperature increases picking by increasing the tack of the ink. Picking is most likely to occur when the press is first started before the ink has warmed up. An ink which prints perfectly at 70° F. may pick at 60° F. Pressrooms which operate only one shift are likely to experience trouble with picking when the presses are first started in the morning. High printing speed increases the tendency toward picking. Large printing areas increase the tendency to tear the paper because of the greater area from which the ink must be pulled. Too rapid oil absorption may create picking due to the sudden increase in tack of the ink resulting from the light varnishes penetrating into the paper. Too thin an ink film may be the cause of pick also, since the cohesion of the ink may be too great in the thin film.

The remedies for picking are to change to a paper with a stronger surface, to reduce the tack of the ink by adding reducing agents (e.g., wax compounds or kerosene), or to change to another less tacky ink. Raising the temperature of the pressroom often helps. Reducing the tack of the ink is a common remedy for picking, but if the strength of the paper is too low, the ink may have to be reduced to the point where mottle and weak printing result. Picking of coated papers can be prevented by using sufficient adhesive in the coating formula, as already pointed out in the discussion of coated papers for relief and offset printing (see also Ch. XVIII). Increasing the amount of ink on the plate will sometimes eliminate picking, particularly if the trouble is caused by the ink drying too fast. If picking occurs in the non-printing areas when printing by the offset process, it may be caused by an oxidized or tacky rubber offset blanket. In this case, the blanket must be corrected, or a new blanket installed. Powdering the blanket with sulfur or washing with carbon disulfide are temporary means of reducing a tacky blanket.

Tinting and Washing

Tinting (bleeding) is the printing of a light film of color on the areas of the paper which should be unprinted. This phenomenon occurs in lithographic printing where it is generally caused by a small amount of ink or pigment dissolving in the water. The only remedy for this trouble is to change to a non-bleeding ink, or to add a heavy, non-bleeding varnish to increase the body of the ink. Bleed is sometimes due to a poorly washed organic pigment in which there is a small percentage of free dyestuff. The addition of barium chloride compound will mordant this dye, removing the bleed.

Washing is a trouble often confused with bleeding. Washing, however, is generally caused by a breakdown of the ink on the offset press resulting from too much water or too strong an acid solution being carried on the dampening rollers. Washing can generally be corrected by adding a longer varnish to the ink or by changing the ink.

Scumming

Scumming or greasing is a trouble occurring in lithographic printing caused by the formation of scum on the printing plate, making it difficult to keep the work open and clean. Scumming can be caused by any one of a number of different conditions.

Scumming is a frequent cause for complaint in the printing of coated papers. Excessive alkali in the coating causes scumming (*1*) by removing the adsorbed gum arabic film from the non-printing areas of the lithographic plate, thus permitting the adsorption of fatty acids in the ink vehicle, or (*2*) by reacting with fatty acids in the ink vehicle to form soaps which destroy the delicate balance between the ink and water systems. Coated papers containing calcium carbonate are most likely to contain excessive alkali, and hence most likely to cause scumming. Reed[95] has shown that the scumming tendency of a coated paper correlates fairly well with the foaming tendency of a water extract of the coated paper, scumming in this case probably being caused by colloidal substances in the extract which tend to emulsify the ink and water on the plate. Extracts from starch-coated papers do not foam as much as extracts from casein-coated papers, but starch-coated papers are not generally used in lithography because of their lack of water resistance. Coated papers lacking in water resistance cause scumming by the coating pigment transferring to the blanket where it acts as an abrasive on the plate so that the plate picks up ink in the non-work areas.

In uncoated papers, the presence of excess alum or chlorides may cause scumming by resulting in deterioration of the printing plate surface. Excessive grit will cause scumming by acting as an abrasive on the plate. Another possibility is the extraction of surface-active agents from the paper.

So far as the ink is concerned, an ink which is too short in body or an ink which contains too much greasy compound will cause scumming. The remedy in this case is to use a longer varnish and to eliminate the greasy compound from the ink.

If scumming is caused by excess alkali, increasing the acidity of the fountain water will be helpful.[96] This remedy can be used in the case of uncoated and certain coated papers, but cannot be used with coated papers containing calcium carbonate. If scumming is caused by excessive wear of the plate, changing to a less abrasive paper will be helpful.

Duplicator Processes

A discussion of printing would be incomplete without reference to the closely related field of duplication. Considerable amounts of paper are consumed each year by government agencies, educational institutions, social and church organizations, and by business and industrial organizations in operations involving one or more of the major duplicating processes now on the market. These processes may be subdivided into five major classes: (*1*) stencil duplicators, (*2*) hectograph or gelatin duplicators, (*3*) spirit duplicators, (*4*) lithographic or offset duplicators, and (*5*) photo-copying duplicators. Most of these methods of duplication require specialized papers, such as special master sheets or copy papers. Carbon papers, one very well-known product used for copying, are discussed in Chapter XXII.

The fundamental economy of duplicating methods coupled with speed, ease of operation, and flexibility have been primarily responsible for their increasing usage. Future developments in duplicating machines and materials, as well as greater demands on the part of the consumer for higher quality, will call on the ingenuity of the paper chemist for the development and production of improved papers. Although considerable research has been done by individual paper manufacturers in the development of duplicator grades, very little material has been published on the specific requirements of papers for this type of work. As a result, the properties of papers used in the various processes are subject to fairly wide variations when the products of individual producers are compared.

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[95] R. F. Reed, *Paper Trade J. 88*, No. 10: 57–60 (Mar. 7, 1929)

[96] R. F. Reed, *Paper Trade J. 102*, No. 22: 281–283 (May 28, 1936)

Stencil Duplicators

Stencil duplicators are among the older methods of producing multiple copies of typewritten or drawn material. There are many models of stencil duplicators. The mimeograph is the best known of these processes and has lent its name to grades of paper normally used for stencil duplication work. The mimeograph process was invented in 1884 and the name "mimeograph" is the trade name for the process of A. B. Dick.

The process consists, briefly, of preparing a stencil and subsequently forcing ink through the stencil openings onto the copy paper as it passes through the duplicating machine. The stencil consists of a fibrous sheet of strong tissue mounted on a tympan backing sheet. The stencil is treated with an ink-resistant mixture composed of nitrocellulose, waxes, fatty acids, and plasticizers.

In cutting a stencil, the stencil is backed up with a second sheet, a sheet of unimpregnated tissue called the stencil cushion sheet, which is placed between the stencil sheet and the backing sheet to cushion the stencil paper. Auxiliary equipment usually supplied by the manufacturer, such as various graining or shading tools and styli, allow the operator considerable freedom in composition and artistic effects. Standardized forms can be mass produced from dies on a printing press, thereby eliminating much tedious hand labor when such forms are applicable.

The duplicating machine consists of a perforated revolving impression cylinder, an ink-feeding mechanism on the inside of the cylinder, a felt blanket or wick which covers the perforated face of the cylinder, a paper infeed, and a delivery. In setting up the cut stencil, the cushion sheet is removed and the stencil hung on the hooks of the cylinder. The upper clamp is closed, the backing sheet is torn off, and the stencil then is laid smoothly on the pad around the cylinder. If the stencil is full length, it is clamped under the bottom clamp. If not, a sheet of paper is placed over the pad to cover the non-printing areas, and the tail of the stencil runs free. During printing, the ink is forced through the openings in the stencil onto the copy paper as it comes in contact with the stencil.

Inks used in this type of duplicator are principally the non-drying oil types very similar to news ink. Drying of the ink is thus dependent on penetration of the ink into the copy. Certain water emulsion inks are also being used in stencil duplicating work at the present time. The type of ink used has a great influence on the properties of the paper required for satisfactory performance with this process. The maximum number of copies obtainable depends upon the stencil, copy, paper, and other factors, but is generally between 2,000 to 5,000 copies per stencil. Speeds vary from 165 to 250 per minute.

Mimeograph papers are a grade of writing or book paper used for making copies on a mimeograph machine. Mimeograph papers usually have a grainy or toothed surface to aid in preventing offset until the ink has had a chance to penetrate the paper. Antique wove paper made from sulfite and soda stock is frequently used. The paper must have a closed formation and possess good absorbency for the ink vehicle. It must have good opacity, be free of fuzz, and, in most cases, be sized for pen and ink writing. Mimeograph papers are manufactured in a full range of colors and in weights from substance No. 16 up through ledger weights, substance No. 20 being most common. The paper is usually loaded or filled with clay or other mineral fillers so that the ash content ranges from 2 to 12%. Bulky, highly oil-absorbent fillers have been used in mimeograph grades to improve the copying characteristics, although the cost of such fillers frequently limits their use.

Hectograph (Gelatin) Duplicators

The hectograph process is very old. It was the only method of duplicating before the introduction of stencil duplicators. The process is still used where the number of copies required is very small and when special color effects are desired. Gelatin duplicators employ gelatin films which receive copy of the image and transfer it to suitable copy paper. The machines range from flat-pad hectographs to modern rotary machines employing specially prepared rolls of paper or fabric coated with gelatin or modified gelatin mixtures. The basic process is, however, the same in all cases.

A master copy of the material to be duplicated is prepared on a special master paper by printing, typing with special ribbons or carbon papers, or by means of special writing inks or pencils. The inks used have a high proportion of water-soluble dyes of high tinctorial strength: After preparation, the master is placed, face down, on the gelatin composition, where it is allowed to remain for a few seconds, thereby transferring the dye to the gelatin. After removal of the master, copy sheets are placed over the same area of gelatin in succession, either manually or mechanically, to obtain the desired copies. From 75 to 150 legible copies can be obtained by this method, depending upon the copy. Inks give the brightest work and longest runs (150 copies), pencil work being used only for short runs of about 75 copies or less. The speed varies from about 12 per minute for hand-operated flat-pad hectographs to 75 per minute for rotary machines.

Reprints can be made by reusing the master as many as eight times. As many as eight colors can be reproduced in one operation by using different masters. The gelatin can be reused after it has been allowed to stand for from four to twenty-four hours between each use.

The papers required for this process can be divided into master papers and copy papers. Master papers are normally strong, chemical wood pulp or rag content sheets, rather heavily tub-sized with starch or starch-glue mixtures. Some parchment is used for pencil work. The master must possess good resistance to ink penetration and must be strong enough to withstand the forces encountered in mechanical stripping from the gelatin mass. Master papers are manufactured in weights ranging from substance No. 13 to No. 24.

Copy papers for the gelatin process are manufactured in weights from substance No. 13 through ledger and index weights. They are made in a full range of colors for coded business systems. The principal requirements for copy papers are sufficient surface strength to prevent peeling or tearing when the copy is stripped from the gelatin, freedom from curl, both before and after duplication, sizing for pen and ink writing, freedom from surface fuzz, and sufficient opacity to prevent show through. Papers for this process are usually loaded with clay, talc, or other mineral fillers, ash contents of 5 to 10% being common. Titanium dioxide is frequently used to improve color and opacity. Most gelatin process duplicator papers are tub-sized with starch or modified starch mixtures. Some special coated papers are produced for short run work where extremely bright copies are desired.

Spirit Duplicators

The spirit or liquid duplicator is a reproduction process in which a master copy is perpared by means of a special carbon paper. The carbon paper used in making the master copy is a special one-time carbon containing a high concentration of a spirit-soluble dye, usually a basic dyestuff, of high tinctorial strength. The master is prepared by making a reverse carbon copy on the back of the master paper, after which the master is attached to the impression cylinder of the duplicating machine. Then, the copy paper, slightly moistened with a special duplicating fluid consisting of a mixture of alcohols, is brought into contact with the master copy. The solvent on the copy paper dissolves sufficient dye from the master copy to produce the impression as a positive image on the copy paper. About 300 to 500 legible copies can be obtained by this process. The speed is about 75 per minute. Carbons are available in purple, red, blue, and green. Purple carbon gives the best results. There are no very good black carbons for spirit duplication because there are no true basic black dyes.

Master papers for spirit duplication are specially prepared, coated papers. Special blocking agents are often added to the coating to prevent bleeding of the oil and dye from the carbon into the paper during standing or storage of prepared masters.

Copy papers for spirit duplication are made in a range of grades, from groundwood content sheets to sulfite bonds. The paper is usually loaded or filled with talc, clay, or other mineral fillers with ash contents varying from 5 to 15%. Titanium dioxide is frequently used as an opacifying agent. Weights range from substance No. 16 through ledger and index grades. A full range of colors is usually stocked. The copy sheets are normally tub-sized with starch or other sizing materials to improve the surface characteristics. The paper need not be as absorbent as other duplication papers, but some absorbency is necessary to carry a controlled amount of duplicating fluid to the master sheet to produce an adequate transfer of the dyestuff to obtain a clear copy. Most grades are sized for pen and ink writing. The relationship between the solvent used in this process and the paper is extremely important in the production of clear copies and long runs. Incompatibility of solvent and paper can produce blurred copies and rapid breakdown of the master sheet.

Lithographic (Offset) Duplicators

Offset duplicators are small offset presses, especially designed for office use. Special paper plates can be used for reproducing written, typed, painted, or drawn image placed on the plate, or regular metal lithographic plates can be used. Parchment papers laminated to a waterproof backing sheet and special pigment-coated papers are used for paper plates. Equipment for the preparation of photo-offset plates is usually supplied as auxiliary equipment by the manufacturer.

The discussion of lithography and offset printing in the previous part of this chapter applies in whole or in part to this form of duplication. Consequently, there is little need to repeat the discussion of ink and paper requirements or press problems at this point. However, one significant difference between offset duplicating and regular lithography is that glycerine is generally used in the fountain solution in the former case to keep the plate moist and prevent drying. Special inks are required for office machines because of this glycerine in the fountain solution.

Offset duplicators operate at speeds up to about 5,000 impressions per hour, but average production is about 4,000 to 4,500 per hour. The maximum number of copies is about 25,000.

Letterpress Duplicators (Multigraph)

Letterpress duplication is done on small rotary relief presses. The process is not, strictly speaking, a duplication process, being more closely related to printing. Hand-set type, stereotypes, electrotypes, or rubber plates can be used. The plates can be inked by regular ink rollers, or printing can be done through an inked ribbon wrapped around the printing cylinder to which the paper is pressed by means of an impression roll.

Letterpress duplication is suitable for the reproduction of typewritten material used for form letters, reports, and advertising matter. It is used for reproducing a large number of copies of material simulating typewritten matter. The speed of operation is 1,000 to 5,000 copies per hour; the maximum number of copies varies from 50,000 to 200,000. The properties of the paper should be the same as those for relief printing. Bond and writing papers are most frequently used.

Automatic Typing

Individually typewritten letters can be produced in quantity by automatic typing at low cost. A master roll or tape working on the principle of the piano roll automatically types the letters, leaving space for address, heading, or special information. These spaces are then typed in by hand later, a near-perfect match being possible. The speed is about 110 to 125 words per minute, and any number of copies can be produced.

Photo-Copying Processes

Photo-copying duplication processes such as direct process and blueprint are used to produce multiple copies of original material. The expense of these processes and the time consumed in making copies usually limits this form of duplication to relatively specialized fields where only a limited number of copies are desired, for example, copies of plans or drawings prepared by architects, engineers, or draftsmen. In the blueprint process, white lines are produced on a blue background, whereas in the direct (diazotype) process, black, brown, red, or blue lines are produced on a white background.

Reproduction by the photo-copying processes is done from original ink or pencil drawings on transparent tracing paper. In making prints, the transparent tracing paper bearing the original drawing is placed on top of the light-sensitive reproduction paper in very close contact and then the assembly is exposed to intense light from a bank of arc or mercury vapor lamps. The light penetrates through the transparent paper and acts upon the layer of light-sensitive chemicals on the surface of the paper. No light passes where there are lines or figures on the tracing paper. After exposure, the tracing paper is removed and the printing paper is developed to bring out the design.

The tracing paper used in making reproductions must have high transparency in order to permit passage of light during printing. Creamy or yellow tracing papers are undesirable, since they tend to block out the light; good tracing papers should be colorless or have a bluish tint.[97] Other requirements of a good tracing paper are good receptivity to drawing inks, high strength (particularly good tear and fold), and good erasing qualities. The paper must have good formation and even caliper. The common weights are 12, 14, 16, and 18 lb. (17 × 22—500). Both unimpregnated and impregnated grades are used commercially. The lines of the drawing on the tracing paper must be heavy enough and sufficiently continuous so that no light penetrates through them during printing to weaken the line on the final print.

Blueprint Process. Blueprint paper is a special grade of paper which has been treated on the felt side with a solution of sensitizing chemicals, i.e., potassium ferricyanide and iron salts such as ferric ammonium oxalate. The solution is applied to the paper on a coating machine, where conditions are controlled to obtain the necessary penetration of chemicals into the paper, after which the paper is dried in the dark.

In making reproductions by the blueprint process, the sensitized blueprint paper is exposed to light through the original drawing on tracing paper. This converts the ferric salt to ferrous salt which reacts with the ferricyanide to produce ferrous ferricyanide which in turn is converted into insoluble blue ferric ferrocyanide. The exposed paper is washed by spraying and by immersion in water to remove residual unexposed chemicals. The paper is then treated with a solution of oxidizing agent (e.g., peroxides or bichromates) and washed to remove excess oxidizing agent. The result is a negative print containing white lines on a blue background.

Rag or rag content sulfite papers are generally used in making the base stock for blueprint papers. The paper must have a fairly smooth surface, good folding endurance, good tearing resistance, and above all, must have a high degree of wet tensile strength and wet rub resistance to withstand the soaking in water during developing. The paper is generally surface-sized with glue which is hardened with formaldehyde in order to develop sufficient wet strength. The paper must be free of all chemicals (e.g., residual formaldehyde left over from surface sizing) which would react with the chemicals in the sensitizing solution or with the oxidizing agents used in developing. The absorbency and sizing of the base paper must be controlled to obtain the correct amount of penetration of the sensitizing chemical in the treating operation. A high opacity is required, and generally the paper is filled with clay or titanium pigment. The color of the paper should be yellowish or pinkish in order to mask the light blue tint left in the undeveloped areas and provide the maximum visual contrast with the blue background.[98] The basis weight is usually 24 lb. (17 × 22—500), although weights from 12 to 30 lb. are used.

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[97] H. Klein, *Paper Trade J. 129,* No. 11: 338–341 (Sept. 15, 1949)

Ordinary blueprints are negatives, but positive blueprints can be made having blue lines on a white background. These are made by first forming a negative print, called a brown print, in the same manner as described above for a blueprint. The brown print, which contains relatively transparent white lines on a dark brown background, is then used as an intermediate negative for making blueline prints on regular blueprint paper. Paper for making brown print negatives must be light in weight (12 to 16 lb., 17 × 22—500), but must be very strong. The paper must be highly transparent so that the light can readily penetrate through the transparent lines of the negative. The brown developed areas must, however, be opaque to prevent the passage of light. In order to obtain a high degree of opacity in the brown areas of the negative, the sensitizing solution is allowed to penetrate deeply into the paper and a long exposure time is used during printing.

Direct (Diazotype) Process. Direct (diazotype) papers are newer than blueprint papers and have replaced blueprint papers to a large extent. Diazotype papers are made by treating the surface of the paper with an acidic solution (usually a *p*H of 2) of light-sensitive chemicals, an attempt being made to obtain only a slight degree of penetration into the paper.

During printing, the sensitized paper is exposed to light through the original drawing, after which the paper is developed. Two developing processes are used, the ammonia and the semi-wet processes. In the ammonia process, all the color-producing agents are present in the sensitized coating on the paper, and developing consists of treating the light-exposed paper to fumes of moist ammonia, which neutralizes the acid present in the coating and permits coupling to take place. In the semi-wet process, the paper is moistened with a strongly alkaline developer solution which contains part of the color-producing components. The final result in either case is a positive print having blue, black, brown, or red lines on a white background.

The base paper used in the diazotype process is generally made from sulfite stock of high purity. The paper is surface-sized with starch or with a mixture of starch and urea-formaldehyde resin if the paper is to be developed by the semi-wet process. Glue-sized papers are not used, because glue produces yellow-brown backgrounds in the tints,[99] and because high wet tensile strength is not required, since the papers are not immersed during developing. The paper should be well sized, and it is desirable that the paper retain its sizing after developing so that notations can be made on the print with ink. Sizing due to rosin is generally destroyed during developing because of the alkaline developing solutions normally used. High opacity and high brightness are desirable properties, and generally diazotype papers are filled with titanium. A pinkish cast is desirable when blue lines are produced whereas a blue-green cast is desirable when black lines are produced; acid- and alkali-resistant dyes are required. The paper should be free of iron. Dirt spots are objectionable since these are not hidden as they are in blueprint papers. As with blueprint papers, high folding endurance is desirable so that the paper can stand up under the repeated handling which it normally receives in use.

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[98] H. Klein, *Paper Trade J. 129*, No. 11: 338–341 (Sept. 15, 1949)

[99] H. Klein, *Paper Trade J. 129*, No. 13: 381–382 (Sept. 29, 1949)

Lithoprints. Lithoprints are made from gelatin on which an exposed, undeveloped blueprint is transferred. The resulting print is black on white. One advantage of this process is that clean copies can be made from dirty originals.

CHAPTER XX

LAMINATING AND PASTING

The operations of laminating, combining, gluing, and pasting are important parts of the paper industry. These operations involve the sticking together of two or more sheets of paper by means of a laminant or glue, with the purpose of producing a laminated structure possessing either increased strength, improved appearance, or greater utility in some other respect.

Laminating Processes

Laminating of paper products is usually carried out in a separate converting plant. Some of the more familiar laminating operations carried out as part of the paper industry are:

(*1*) Lamination of two to five plies of paper, usually either kraft or jute, into a thick paperboard which is suitable for solid fiber shipping cases. This process is generally known as solid fiber laminating.

(*2*) Combination of kraft or jute liner stock with a corrugated sheet of straw, kraft, or semichemical to produce corrugated paperboard for use in manufacture of corrugated shipping containers. This process is known as corrugating.

(*3*) Lamination of a thin sheet of high-grade paper to chipboard to produce a more attractive board for fancy boxes. This process is called sheet lining.

(*4*) Lamination of a special sheet such as glassine paper or greaseproof paper to another dissimilar sheet or to chipboard to produce a final product which has special properties. In this process, one or more of the units may be some material other than paper, such as lead foil, aluminum foil, copper foil, cellophane, cellulose acetate, Pliofilm, or polyethylene sheeting. A frequent combination is 0.00035-in. aluminum foil laminated to a 30-lb. sulfite sheet used for greeting cards, box coverings, seals and labels, and as a liner for cigarette packages.

All the above are continuous processes in which the paper is fed in roll form through the laminating machine. The first step in the operation is the application of adhesive to the paper, after which the various plies are pressed together to produce the laminated board. The combined board is then passed over driers and finally cut to the desired size at the end of the machine. There is another process called sheet pasting in which small sheets of paper or paperboard are fed by hand through a set of rolls which apply paste to each sheet individually, after which the pasted sheets are combined by hand.

As previously mentioned, it is not the function of this book to discuss engineering details. This policy will be followed in this chapter, and no attempt will be made to discuss the various types of laminating machines. There are, however, certain general mechanical principles with which the chemist should be familiar, because if these principles are not understood, a satisfactory job of laminating cannot be done. In fact, the method of applying and setting the adhesive is as important, or more important, than the properties of the adhesive itself. The amount of glue applied to the paper, the temperature of the glue, the amount of pressure applied to the glued assembly, and the time allowed for the setting of the glue are all extremely important factors. All laminating machines should be kept in the best possible condition. The glue applicator rolls should be smooth and absolutely true, because otherwise, uniform glue lines will not be obtained. The pressure rolls should also be true and smooth to provide uniform pressure across the laminated sheet. Some means of temperature control should be provided in order to control the viscosity and penetrating properties of the adhesive.

Types of Adhesive Used

Many types of adhesives are used in laminating paper. These include: (*1*) aqueous adhesives such as animal glue, starch, silicate of soda, and casein; (*2*) hot-melt adhesives such as asphalt and wax; (*3*) lacquer type adhesives such as cellulose nitrate dissolved in organic solvents; and (*4*) emulsion type adhesives such as polyvinyl acetate emulsified in an aqueous medium. Special adhesives, which may fall in one or more of the above groups, are water-resistant adhesives, heat-seal adhesives, and pressure-sensitive adhesives. In addition, adhesion between plastic bodies may be obtained by heat-molding or by solvent welding.

Aqueous versus Non-Aqueous Adhesives

Up to fairly recent times, nearly all adhesives used in the paper industry belonged to the class of aqueous adhesives, represented by the starches, vegetable gums, casein, blood glue, sodium silicate, and animal glue. However, within recent years, the newer lacquer adhesives, emulsion type adhesives, and hot-melt adhesives have gained ground, principally for specialized uses. With these new adhesives, it is possible to obtain special properties such as water-proofness, alkali-proofness, water-vapor-proofness, gas-proofness, or grease-proofness, which cannot be obtained with the older types of glue. On the other hand, there are certain disadvantages to these new glues. Many of them are too expensive for ordinary use. Furthermore, some have undesirable odors which make them unsuited for food packaging. The use of all these adhesives will be discussed in greater detail later in this chapter.

Water-Resistant Adhesives

For many purposes, it is necessary or desirable to use an adhesive which produces a water-resistant bond. Some of the laminated products requiring water-resistant adhesives are solid fiber paperboard for use in overseas shipping containers, solid-fiber paperboard for use in beer cases, and paperboard for beverage bottle cartons. In addition, water-resistant adhesives are required for gummed labels used on medicinals, toiletries, etc.

Lacquer or hot-melt adhesives are the most satisfactory types when maximum water resistance is desired, because these non-aqueous adhesives provide complete protection against water. Some of the resin emulsion adhesives also produce highly water-resistant bonds. Among the natural adhesives which produce water-resistant glue lines are the casein glues, blood glues, soybean glues, and other protein glues. On the other hand, starch adhesives, as a rule, do not produce water-resistant bonds, although they can be made water-resistant by using urea-formaldehyde resins in combination with the starch. Sodium silicate has very poor water resistance because of its high alkalinity, which tends to destroy the sizing in the paper, thus producing a water-sensitive area in the paper just below the glue line.

Heat-Seal Adhesives

Heat-seal adhesives are usually applied as a coating which in later combined to another surface by melting the adhesive with heat. There are two types, the direct contact type, and the delayed action type. In the direct contact type, heat is applied after the coated adhesive surface has been brought into contact with another paper surface. In the delayed action type, the adhesive surface is heated and activated before the two surfaces have been brought into contact.

Heat-seal adhesives are available in emulsion, hot-melt, and lacquer types. Paraffin is used as a heat-seal adhesive in waxed bread wrapper, where it is common practice to seal the wrapper by placing the two ends of the wrapped loaf between two heated platens. This melts the wax, which forms a seal when the loaf is removed and cooled. Cooling is necessary with heat-seal adhesives based upon wax, but lacquer type and emulsion type adhesives tend to fuse immediately upon the application of heat.

It is interesting to note that two different adhesives will not heat-seal with each other unless they have chemical similarity: e.g., ethyl cellulose will not heat-seal with polymethacrylate, although either one makes a good heat seal by itself. Some examples of heat-seal adhesives are as follows:

(*1*) Plasticized cellulose derivatives, such as ethylcellulose and cellulose nitrate.
(*2*) Rubber derivatives, such as cyclized rubber and synthetic rubbers.
(*3*) Polyisobutylenes.

(*4*) Polyvinyl resins such as polyvinyl chloride acetate copolymer, polyvinylidene chloride and copolymers, polyethylene, and acrylics.

(*5*) Polyamides.

Usually, a plasticizer is necessary in the formulation to obtain the best heat-seal properties. One patent[1] calls for a coating on cellophane consisting of polyvinyl acetate, cellulose nitrate, and diethylene glycol monomethyl ether. The subject of heat-seal adhesives is discussed further later in this chapter, and also in the chapter on coating with resinous materials.

Pressure-Sensitive Adhesives

The adhesives on Scotch tape and masking tape are examples of pressure-sensitive adhesives. Pressure-sensitive paper tapes are made of several layers composed of the base paper, a primer coat on the paper, and a layer of pressure-sensitive adhesive. On the other side of the base paper, it is necessary to have a layer of some material which is repellent to the adhesive in order to prevent the adhesive from sticking to the paper when the tape is wound into a roll. A layer of cellulose acetate is usually satisfactory for this purpose.

Among the materials which may be used in pressure-sensitive adhesives are rubber and rubber derivatives, synthetic rubbers (GR-S, neoprene, and polyisobutylene), alkyd resins, ethylcellulose, rosin derivatives, acrylic resins, other vinyl resins, and the natural resins. Rubber has been widely used, and one satisfactory formula consists of a mixture of chlorinated rubber, a plasticizer such as castor oil, and a solvent such as butyl acetate. Another formula is represented by 20% of rubber, vinyl resin, or ethylcellulose; 40% hydrogenated methyl abietate; 40% rosin, dammar resin, or coumarone-indene resin. Another formula is represented by a mixture of polyvinyl chloride-acetate copolymer and Buna N rubber, together with methyl ethyl ketone as a solvent.

Solvent Welding

The solvent welding of plastic surfaces is not widely used in the laminating of paper products, but it is of interest to a student of adhesive action. Solvent welding can be used only for the laminating of solvent-soluble plastic bodies. In this method of laminating, a solvent is used to soften two sheets of plastic materials which can then be welded into a strong joint as the solvent diffuses away from the joint. This method of welding is satisfactory only if substances of similar nature are welded, since dissimilar substances will not form a strong bond, even though the welding agent is a solvent for both. For example, acetone will weld two sheets of cellulose acetate, but will not produce a strong bond between a sheet of cellulose acetate and a sheet of cellulose acetate-butyrate, even though acetone acts as a solvent for both substances.[2]

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[1] J. A. Mitchell, U. S. 2,374,767 (May 1, 1945)

Heat Welding

Heat welding is another method of combining surfaces when mutually compatible polymers are involved. In this process, heat is used to soften the surfaces so that they can be welded into a continuous joint. Only plastic bodies which soften under heat can be used for heat welding.

Theory of Adhesion and Adhesive Properties

Before discussing the subject of adhesion, it is necessary to understand what constitutes an adhesive. Actually, it is very difficult to define an adhesive, since almost any substance will act as an adhesive under certain circumstances. A classical example is the strong adhesive effect which is obtained with a thin film of water between two pieces of clean plate glass. In general, however, an adhesive may be defined as any fluid which will "wet" the two surfaces to be combined and which can then be converted into a tough mass by cooling, evaporation, etc., so that the two surfaces are held together with appreciable strength. A good adhesive should have a modulus of elasticity comparable to that of the materials laminated.

Paper is a particularly easy material to combine with adhesives because of its porous structure which permits a high degree of interlocking or mechanical adhesion. As a result, the lamination of paper is not a particularly difficult proposition. However, laminating some of the newer materials, such as waxed papers, impregnated papers, synthetic resin sheeting, and coated papers often involves considerable difficulty. The introduction of these new materials has greatly increased the complexity and difficulties of laminating problems. The lamination of these materials involves a form of adhesion known as specific adhesion.

Specific Adhesion

There is no universal glue which will work on every surface. On the contrary, all adhesives are more or less specific for a particular surface. A strong bond can be formed only if there is a similarity in molecular structure between the adhesive and the surface to be joined. For example, highly polar adhesives (starch, animal glue, etc.) make excellent adhesives for paper because paper is highly polar. On the other hand, strong bonds cannot be produced when polar adhesives like starch are used on non-polar surfaces such as those presented by waxed paper, unless the continuity of the wax film is first partially destroyed with solvents. As another example of the effect of polarity, it can be shown that increasing the number of polar hydroxyl groups in polyvinyl acetate through hydrolysis will increase the adhesiveness of this material for polar surfaces.

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[2] J. Del Monte, *The Technology of Adhesives,* Reinhold Publishing Corporation, New York, N. Y. (1947)

Specific adhesion is due to molecular attraction (electrostatic, covalent, or residual binding forces of the van der Waal's type) between the adhesive and the surfaces joined. The bonds which are produced are often tremendously strong, and it is possible (with very thin films of adhesive) to obtain bonds which are stronger than the tensile strength of the adhesive itself. This is apparently due to fields of force from the opposing surfaces being superimposed upon the ordinary cohesive forces within the adhesive film in such a way that they strengthen the cohesiveness of the glue.

In order for adhesion to take place, the adhesive molecules must come into close contact with the surface of the materials to be adhered so that molecular forces can come into play. Molecular nearness is accomplished by formulation of the adhesive so that the molecules of adhesive are in a highly mobile state at the time of application. This is done by applying the adhesive in a solvent, in a molten state, or in an unpolymerized form so that it can be subsequently polymerized in place.

Adsorption phenomena probably play an important part in specific adhesion. In fact, Bancroft[3] believes that the degree of adhesion can, in many cases, be measured by the amount of adsorption of adhesive on the material laminated. Considerable work on the fundamentals of specific adhesion has been carried out at the U. S. Forest Products Laboratory.

One of the important differences between specific and mechanical adhesion is that adhesives which act by specific adhesion are effective on nonporous, as well as porous, surfaces, whereas adhesives which function by purely mechanical means are effective only on porous surfaces. Thus, specific adhesion is all-important in the lamination of metal foils, coated cellophane (MST, MSAT), cellulose acetate, coated glassine, and other similar non-polar and non-porous materials. It is probably a factor with such semiporous materials as glassine, uncoated cellophane (PT), and vegetable parchment. Wet-strength papers are more difficult to laminate than ordinary papers, and this may be due to lower specific adhesion. Some of the newer transparent plastic sheetings (e.g., Saran, Pliofilm, and particularly polyethylene) are very difficult to laminate and require specialized adhesives having a high degree of specific adhesion.

Mechanical Adhesion

Mechanical adhesion differs greatly from specific adhesion. It is a much simpler concept and involves a keying of the adhesive into the pores of the laminant. Mechanical adhesion is particularly important on paper, inasmuch as paper is highly porous and permits considerable penetration and solidification of the adhesive around the fibers. A very strong bond can be formed by this mechanical embedding of adhesive in the pores of the paper. Glued wooden joints also appear to be held together by mechanical adhesion.[4] McBain and coworkers[5] in England have been among the principal proponents of the mechanical theory of adhesive action.

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[3] W. D. Bancroft, *Applied Colloid Chemistry*, p. 74, McGraw-Hill Book Company, New York, N. Y. (1921)

In cases in which mechanical adhesion predominates, it is necessary that the adhesive have the proper viscosity to flow into the pores of the laminant or a good bond will not be obtained. The adhesive should then solidify in place to produce an interlocking system. Penetration is the important factor, and either too much or too little can result in an inferior glue joint.

Effect of Adhesive Properties

Most adhesive materials are high polymers. Each adhesive has an optimum molecular weight for best adhesive action, and this is usually in the intermediate range of molecular weight. Too high a molecular weight is undesirable because it leads to high viscosity, low solubility in solvents, and reduced adhesive strength. On the other hand, too low a molecular weight is undesirable because it means that the adhesive is likely to have insufficient cohesive strength to hold the assembly together. Thus, starches are modified to products of intermediate viscosity before conversion into adhesives. By the same token, animal glues of medium jelly strength are usually selected for adhesive purposes. Thermoplastic polymers also have their best adhesive action at an intermediate degree of polymerization where the resin has good specific adhesion for the surfaces to be joined and enough cohesive strength to form a strong assembly. According to Del Monte,[6] the range of polymerization best suited for good adhesive action for a number of different synthetic resin adhesives is as follows:

Type of adhesive	Degree of polymerization
Polyvinyl acetate polymers	60–200
Polyvinyl chloride-acetate	100–150
Polyethyl acrylate	80–150
Polyisobutylene	50–150
Polyamides	50–100
Chlorinated rubber	125 cps. viscosity grade
Cellulose nitrate	150–300

In laminating with thermosetting resin glues, the resin increases in molecular weight during the curing cycle, tending to pass through the state of maximum adhesiveness into the state of maximum cohesiveness. This may, in the case of strong assemblies, lead to a weakness at the interface between the adhesive and the surfaces joined. The number and type of substituent groups and the number and type of side chains are other important factors which govern the polarity, solubility, chemical compatibility, and viscosity characteristics of resinous adhesives.

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[4] *Second Report of Adhesives Research Committee,* Dept. of Scientific and Industrial Research, 16 Old Queen Street, Westminster, England

[5] J. W. McBain and W. B. Lee, *Proc. Roy. Soc. (London) A113:* 606–620 (1927)

[6] J. Del Monte, *The Technology of Adhesives,* Reinhold Publishing Corporation, New York, N. Y. (1947)

Viscosity of Adhesive. The viscosity of the adhesive must fall within certain definite limits, depending upon the type of adhesive and the surface to which it is applied. If the adhesive is too viscous, it will make poor contact with the paper surface, whereas if it is too fluid, it will be sucked into the pores of the paper, thereby producing a starved joint. In either case, an improper film results, and the bond is weak. The viscosity is also important in regulating the amount of adhesive transferred from the glue rolls to the paper. Low viscosity permits orientation of the adhesive in the glue joint.

The viscosity of an adhesive can be controlled in one of three different ways. These are: (*1*) by changing the degree of polymerization of the adhesive material itself, (*2*) by changing the type or amount of solvent used in formulating the adhesive, or (*3*) by changing the temperature. In practical operation, the viscosity is controlled by regulation of the amount of solvent in the adhesive. The adhesive may be diluted with solvent to produce a more fluid paste, or part of the solvent may be withheld during preparation if a higher viscosity is desired. This, of course, changes the solids content of the paste, as well as the viscosity of the paste. With starch adhesives, and other adhesives available in several degrees of conversion, it is possible to select products which give quite a range of viscosity at the same solids content. In the case of resins, it is possible to apply high-viscosity materials in a low-viscosity form by emulsifying in water. Low-viscosity pastes are best suited for highly sized papers, whereas high-viscosity pastes are best suited for slack-sized papers.

Increasing the temperature of the paste nearly always lowers the viscosity. This is particularly true of the colloidal adhesives such as starch, glue, casein, and vegetable gums with the notable exception of methylcellulose, which tends to form a gel at high temperatures. The temperature-viscosity relationship is, of course, of paramount importance in hot-melt adhesives.

The type of adhesive flow is important. The practical adhesive user recognizes this fact in a qualitative fashion by designating adhesives as either long or short. A short paste is one with a high yield value and a high mobility, whereas a long paste is one with a low yield value and a low mobility. The paste mixer examines his paste for these qualities by watching how the paste runs off a stick or paddle.

Tackiness of Adhesive. Tackiness is a measure of the adhesive quality and refers to the stickiness or gumminess of the paste. Tackiness implies a combination of factors such as plasticity, adhesion, and cohesion. A tacky paste is usually one with a low yield value and a high mobility. Although there is no satisfactory method of measuring tackiness quantitatively, an experienced paste mixer can obtain an indication of the tackiness by working the paste between his thumb and forefinger and measuring the tendency of the paste to string out when the fingers are pulled apart.

The practical glue user prefers a tacky adhesive, or one which will string out and exert a definite pull. Actually, however, tack is not an essential requirement for a good glue, since some of the strongest adhesives are non-tacky. For example, many of the modern synthetic resin adhesives show no tackiness at the time of application, yet they form very strong bonds on drying. On the other hand, corn syrup and molasses are examples of substances which are extremely tacky, but which have low adhesive strengths. Tackiness is of most importance with starch and dextrin adhesives.

The practical advantage derived from the property of tack is that highly tacky adhesives hold the surfaces together while the glue is still in a wet or fluid condition. If the adhesive is non-tacky, the surfaces to be joined must be held in contact until the glue has dried or set. After the glue has finally set, tack is no longer an important factor.

In general, tackiness increases as the concentration is increased. With most glues, tackiness increases as the temperature is raised to a certain point. Starch or dextrin glues generally have very little tackiness unless borax is present. The addition of clay increases the tackiness of some glues.

Pressure-sensitive adhesives have a lingering tack. These adhesives have extremely high viscosity and derive their adhesive strength from plastic flow.[7] The strength of the bond produced with these adhesives depends upon the rate of pull.

Other Properties of Adhesive. There are many properties of the adhesive which are important from a practical standpoint. Some of these are solids content, wetting properties, type of solvent, alkalinity, and setting rate. The properties of the adhesive which promote penetration are long wet life, small angle of contact, low viscosity, and low surface tension.[8] The properties which inhibit penetration are high viscosity, short wet life, high surface tension, and large angle of contact. The characteristics of individual adhesives will be discussed later.

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[7] H. Green and R. N. Weltmann, *Ind. Eng. Chem., Anal. Ed. 15,* No. 3: 201–206 (Mar. 15, 1943)

[8] F. Camps-Campins, *Paper Trade J. 110,* No. 8: 107–109 (Feb. 22, 1940)

Effect of Sheet Characteristics

A rough surface is beneficial in increasing the amount of mechanical adhesion. On the other hand, a rough surface is undesirable when specific adhesion is involved, because thicker adhesive films are required on rough surfaces. Excessively rough surfaces are undesirable in all cases since they increase glue consumption and there is the possibility of trapping air bubbles in the glue line.

If adhesion is due primarily to specific adhesion, it is necessary only that the adhesive wet the surfaces to be joined. If the attraction between the adhesive and the surfaces to be joined is low, specific adhesion will be poor and a weak bond will be formed. Anything which improves the wetting of the adhesive for the laminant will improve the adhesion. Papers containing a small amount of moisture are more easily laminated with aqueous adhesives than absolutely dry papers, because the paper with the higher moisture content is wetted better by the adhesive. Surface-active or wetting agents are sometimes used in aqueous glues to increase the wetting, particularly for papers which are highly sized with rosin or wax. The addition of asphalt or wax emulsions to aqueous adhesives helps in the lamination of asphalted or waxed papers.

Ordinarily, starch or animal glue adhesives are not satisfactory for laminating highly waxed papers, because of poor wetting. However, it is possible to produce a fairly good bond by emulsifying a small amount of carbon tetrachloride, benzol, or ethylene dichloride in the adhesive. About one-third quart of benzol per gallon of adhesive will greatly improve the adhesion of starch adhesives for paperboard which has been given a wax finish on the calenders. The solvent acts to dissolve the protective film of wax, thus permitting the starch to make better contact with the surface of the paper.

Most solid surfaces are contaminated with films of adsorbed gases, grease, oxides, etc. These films tend to interfere with adhesion and, in some cases, must be removed for best results. Although these films are of no practical importance on paper products, they are sometimes an important factor in the lamination of metal foils. A practice sometimes used to overcome the difficulties of bonding to metal surfaces is to apply a primer coat to which the adhesive is more receptive.

The porosity of the surfaces to be laminated is probably the most important single factor in the penetration and drying of the adhesive. Ordinarily, a certain degree of porosity is desirable in order to conduct away the mobile or liquid part of the adhesive. The removal of water from aqueous adhesives by diffusion through the capillary pores of the paper results in a quick development of tack and a rapid setting of the glue joint. However, too high a porosity results in a starved joint. Camps-Campins[8] lists the following values for the porosity of papers commonly used in laminating. The porosity is expressed as the number of cubic feet of air space per cubic feet of air-free paper.

Glassine	0.15
Bond, book paper (low bulk)	0.5
Bond, book paper	0.7
Jute	0.9
Chipboard, newsboard	1.1
Water-finish Fourdrinier kraft	1.4
Steam-finish Fourdrinier kraft	1.6
Dry-finish Fourdrinier kraft	2.0

Papers of high density (0.1–1.0 in above table) inhibit penetration of the solid portion of the adhesive, but tend to remove the liquid fraction of the adhesive from the glue line more rapidly than low-density papers because of the greater contact between the adhesive and paper surface. This partly explains why a given adhesive will set faster on smooth-surfaced jute than on rough-surfaced kraft. In order to obtain best results in laminating, the penetrating properties of the adhesive must be matched with the porosity of the paper.

At least two surfaces must be considered in laminating. If these surfaces vary in smoothness, porosity, etc., the problems in laminating are greater than if similar surfaces are involved. Some of the combinations frequently encountered are as follows:

(*1*) A hard surface to a hard surface, such as the lamination of glassine paper to cellophane in the manufacture of transparent wrappers for foodstuffs.

(*2*) A hard surface to an open or porous surface, such as the lamination of metal foil to a sulfite sheet in the manufacture of candy or gum wrappers.

(*3*) An open or porous sheet to another porous sheet, such as the lamination of kraft paper to sulfite paper in the manufacture of heavy wrapping or packaging paper.

Each of the above combinations presents a different problem and requires a different type of adhesive.

Other important properties are moisture content, degree of sizing, and temperature of the paper. Increasing the moisture content increases the penetration of aqueous adhesives. The temperature of the paper is important, because cold paper stock tends to reduce the penetration of emulsoid glues by bringing about rapid increase in their viscosity. For this reason, it is desirable to control the temperature of paper used for laminating. Often there is considerable difference in temperature between stock which comes directly from the mill and stock which has been stored in a cold warehouse.

[8] F. Camps-Campins, *Paper Trade J. 110,* No. 8: 107-109 (Feb. 22, 1940)

Application and Setting of Adhesive

When the adhesive is first applied, there is some penetration of adhesive into the pores of the paper. This is desirable, since it increases the area of contact and strengthens the layer of paper just below the glue line. Too much penetration must be avoided, however, since this leads to a starved joint.

In order to secure good adhesion, pressure must be applied to the assembly to bring the adhesive into contact with the paper surfaces and control the amount of penetration. Pressure is necessary when rough-surfaced papers are used, but excessive pressure should be avoided. Too much pressure must not be used on porous papers, since this forces too much of the wet glue into the paper, thereby leaving too little to function as a glue film. Too much pressure must not be used on non-porous surfaces, since this results in glue squeezing out at the sides of the assembly. For best results, the press rolls on the laminating machine should be independent of the glue applicator rolls in order to provide independent control of pressure on the wet film.

It is possible to make an arbitrary but useful distinction between two fairly distinct setting stages. The first stage occurs when the adhesive forms an initial or wet bond which is sufficiently strong to withstand all ordinary handling. The second stage is represented by the formation of the final or dry bond, which is often much stronger than the paper itself. It is the wet bond which determines the setting rate, since the final or dry bond may not be formed until some later time. The length of time which must elapse before the laminated product can be handled determines the speed at which the laminating machine can be operated. If the adhesive is fast setting, the machine can be operated at high speed, whereas if the adhesive is slow setting, the machine must be operated at a low speed.

There is no relation between the strength of the initial or wet bond and the strength of the final or dry bond. In fact, it sometimes happens that a tacky adhesive will produce a strong wet bond, but only a relatively weak dry bond. For example, dextrins generally produce very tacky films, but their dry bonds are often quite weak, although they are strong enough to stick rag content papers to the point of fiber failure when good envelope dextrins are used. On the other hand, pastes prepared from cooked native starch have relatively low wet bonding strength, but form an extremely strong dry bond and, for this reason, are used in the pasting of kraft paper bags.

Adhesives are set by one or more of the following mechanisms: by gelation due to cooling (e.g., hot melts), by gelation caused by heating (e.g., starch glues for corrugating), by gelation due to evaporation (e.g., ordinary starch and silicate glues), and by gelation due to chemical reaction (e.g., catalyzed resin adhesives). These methods of setting are discussed briefly in the following sections.

Setting of Adhesive by Solvent Loss. Most adhesives are set by loss of solvent, either to the atmosphere or by absorption into the paper. As a general rule, the rate of development of film strength in the glue line is directly related to the rate of solvent removal. In cases where the adhesive is applied to relatively non-porous surfaces, there may be a high retention of volatile solvent left in the glue line, which is undesirable because it reduces the cohesive strength of the adhesive film.

As solvent is removed from the glue line, the adhesive film increases in viscosity (and tackiness) and eventually sets to a plastic-like solid. Resin emulsion glues and lacquer type adhesives set rapidly because they readily release solvent to the paper stock. Starch adhesives set more slowly because they tend to release water only gradually. Dextrin adhesives and silicate adhesives set fairly readily because they increase greatly in viscosity upon the removal of only a small amount of water.

Increasing the temperature of the paste increases the rate of solvent removal because of more rapid absorption of solvent by the paper. On the other hand, high moisture content, high density, and a high degree of sizing in the paper tend to reduce the rate of solvent removal. A long air draw before the pasted sheets are brought into contact with each other tends to increase the setting rate by increasing the loss of solvent to the atmosphere. Too long an air draw must not be used, however, since the adhesive film may become too dry to maintain satisfactory contact with the second ply.

Setting by Gelation Due to Cooling. Setting by cooling can be used for starch glues which have a strong tendency to gel on cooling. The glue is applied to the paper at a high temperature (160–190° F.) at which it is quite fluid, but as soon as the hot glue contacts the relatively cool paper, it begins to gel. The next ply of paper is brought into immediate contact so that the bond starts to form immediately. This process is suitable only for highly sized paperboards.

Setting of the adhesive through cooling is used in hot-melt adhesives. In this process, the molten adhesive, paraffin, or microcrystalline wax, is applied to the paper and then is chilled immediately to set the glue joint.

Setting by Chemical Reaction. The mechanism of setting by chemical reaction is typified by catalyzed resin glues which are applied to the paper and then are set by a combination of time, temperature, and *p*H. Generally speaking, these resins form a wet bond long before the chemical reaction is complete and before the glue line reaches its final state. One type of catalyzed glue is that composed of starch, urea-formaldehyde resin, and ammonium chloride catalyst. This type of glue will be discussed later. With catalyzed resin glues, the *p*H of the paper stock is quite important, since it influences the curing of the resin. For the starch-resin-catalyst combination just mentioned, the paper stock should have a *p*H below 7.

Setting by Gelation Due to Heating. Most glues are set more rapidly at high temperature than at low temperature, due to the greater loss of solvent at the higher temperature. However, with starch adhesives for corrugating, heat is used in a different way to bring about a rapid setting due to gelation of the starch. In this process, uncooked starch is used as the adhesive, and heat subsequently is applied to the assembly to cause immediate gelling of the starch. This forms a strong wet bond which holds the plies together until the glue film loses moisture and forms a permanent dry bond. Actually, the dry bond is probably not completely formed for a considerable time after the board is removed from the machine. This process will be described in greater detail later.

Properties of Adhesive Film

The thickness of the glue film is important because of its effect on the cost of laminating and because of its effect on the strength of the laminated product. As a rule, thin films of adhesive produce stronger assemblies than thick films.[10-12] Schumman[13] reports that the strength of the assembly increases as the thickness of the glue film is reduced down to a millionth of an inch, when the glue is applied to optically flat surfaces. However, when rough-surfaced papers are involved, relatively thick films must be applied to obtain good contact between the adhesive and surfaces joined. In this connection, it has been found that stronger assemblies can be obtained by applying adhesive to both surfaces to be joined, rather than to one surface only. Del Monte[14] reports that aqueous adhesives form bonds which are independent of glue line thickness, but that solvent type adhesives show a marked drop in strength with increase in film thickness. One explanation for the greater strength of thin glue lines is that there is less likelihood of flaws in thin glue lines than in thick ones. There are, however, other factors involved, such as the superimposition of stray fields of force from opposing surfaces on the ordinary cohesive forces of the glue and the effect of dimensional changes in the glue line.

In addition to film thickness, there are many other physical properties of the glue film which are of importance. Among these are shear strength, tensile strength, compressive strength, modulus of elasticity, and creep rate. These factors are often of paramount importance in the lamination of metal

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[10] *J. Chem. Ind.* *43:* 165 (1924)

[11] *J. Phys. Chem.* *29:* 188 (1925)

[12] J. W. McBain and W. B. Lee, *Proc. Roy. Soc.* (*London*) *A113:* 606–620 (1927)

[13] R. Schumman, *J. Applied Phys.* *13:* 235–245 (1942)

[14] J. Del Monte, *The Technology of Adhesives*, p. 333, Reinhold Publishing Corporation, New York, N. Y. (1947)

foils and plastic films, but are of lesser importance with paper where the strength of the glue film is ordinarily much greater than that of the paper. For example, a pull of 2 p.s.i. is sufficient to tear the surface of paperboard, whereas the utlimate tensile strength of dried silicate glue lines is in the neighborhood of 750 p.s.i.[15] As a rule, there is enough margin of safety in the strength of glue lines so that any rupture takes place within the paper itself. However, in sealed waxed papers, the tensile strength of the wax film is lower than that of the paper, and in this case, a weak film is desirable because the package must be capable of being easily opened. Another example where a weak bond is desirable is in glues for palletizing multiwall bags or paper boxes in a unitized stack where the individual units must be separated later without tearing the paper. Masking tapes require weak bonds so that the tape can be removed later. These tapes may be removed under small loads if the pull is steady and slow, but even then, they are sometimes stronger than paper.

In making strong assemblies with metals or plastics, one of the most important properties is the modulus of elasticity (stress-strain characteristics) of the glue, or the ability of the glue to distribute loads from one surface to the other. In general, a modulus of elasticity comparable to that of the materials being laminated is desirable. Creep is important with adhesives which tend to migrate under stress. This condition often arises in hot-melt adhesives which contain a high percentage of plasticizer and are soft.

Dimensional changes in the adhesive film are a factor in adhesion because they lead to stress concentrations between the adhesive film and the adhering surfaces. Dimensional change may result from loss of solvent, chemical changes in the adhesive, changes in temperature, changes in moisture content, or variations in applied pressure.

The tensile strength of the glue film is quite important, but often of lesser importance than the specific adhesion between the glue and the surfaces of the laminant. However, in laminating with thermosetting resin adhesives, the resin, which increases in molecular weight during the curing cycle, passes through a state of optimum adhesiveness to a final state of optimum cohesiveness. Thus, when the adhesive is fully cured and has its maximum cohesive strength, adhesive failure in strong laminants (but not with paper products) is likely to occur at the interface.

Curling and Warping

Curling and warping are frequent causes of complaint in laminating operations. Curl is sometimes noticeable at the time of laminating, but more often, it is not apparent until the laminated product has been cut into sheets and dried. In extreme cases, the laminated product may curl into a cylindrical tube which defies all attempts at flattening.

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[15] E. R. Boller, J. G. Lander and R. Morehouse, *Paper Trade J. 110,* No. 12: 167–176 (Mar. 21, 1940)

Curling and warping are the result of uneven expansion in the various plies of the laminated product, generally caused by the uneven absorption of moisture from the wet glue. If the two outside plies of the assembly are of different composition, curl is more likely to occur than if the same paper is used in both outside plies. As a rule, aqueous adhesives give the most trouble. Non-aqueous adhesives, such as the hot melt and lacquer adhesives, are not troublesome because the solvents used do not swell the fibers in the paper. When aqueous adhesives are used, the less water used in the glue, the less the chances of excessive curl, and for this reason, high-solids adhesives (e.g., 40 to 50% solids) are generally preferred when curl is a problem. Plasticizers in the adhesive are helpful in preventing curl, and when properly plasticized adhesives are used, trouble with curl can be greatly reduced, and often eliminated entirely. As examples, it might be pointed out that glassine has been pasted to 0.02 chip using an adhesive of 11% solids, and litho has been pasted to chip, using an aqueous glue of 23% solids, and in both cases, absolutely flat assemblies were produced because the adhesives were properly plasticized.

When two dissimilar sheets are used in the outside plies and curling cannot be prevented by any other means, one expedient is to moisten the outside surface of one of the sheets with silicate or starch solution in order to equalize the expansion before the sheets are laminated. The silicate or starch should be applied to the surface away from the curl so as to resist the force of curl in the opposite direction. This is helpful in many cases, but it will not work if the outside surface of the paper has been waxed or treated in any way to resist the penetration of the moistening agent. Other suggestions for reducing curl are as follows:

(*1*) Apply the adhesive at room temperature.

(*2*) Apply as thin a film of adhesive as possible. Do not use adhesives which are too viscous to spread in thin films.

(*3*) Use papers which have a smooth surface and are neither too soft nor too absorbent.

(*4*) Use papers which have their machine direction and cross direction strengths as nearly equal as possible.

(*5*) In laminating two-ply paper where the curl is away from one ply, run that ply wetter and the other ply drier.

(*6*) Inspect the laminating machine to see that the pressure is even, that the drying is not too rapid, and that there is no uneven tension on the paper at any time.

Aqueous Adhesives

The emulsoidal type adhesives which are dissolved in water constitute the largest class of adhesives used on paper products. Among the most important adhesives in this class are dextrins, starches, casein, vegetable gums, sodium silicate, animal glue, fish glue, and soy flour. These do not include the emulsion type adhesives, which are discussed in a separate section.

The manufacture and formulation of aqueous adhesives is a very complicated business about which the average person outside the business knows very little. Ingredients in great variety are used to modify the base material, including wetting agents, penetrating agents, fluidifying agents, setting agents, preservatives, extenders, and waterproofing agents. Clays, for example, are sometimes added to increase the solids content of the liquid glue, which hastens the drying rate. Clay also prevents excessive penetration of adhesive into the paper and is used in adhesives for porous papers and paperboards.

Starch and Dextrin Adhesives

Starch and dextrin adhesives constitute one of the largest class of aqueous adhesives used in the paper industry. Starch is used in practically all degrees of modification, ranging from unmodified native starch to highly converted dextrins. Enzyme-converted starches are used to some extent. The same general procedure is followed for enzyme conversion as in other starch applications, except that high percentages of enzyme must be used because of the high solids. The procedure is very similar to that used in the conversion of starch for pigment coating.

Most starch adhesives contain from 5 to 20% borax which is added to increase the tackiness of the paste. Too much borax, however, increases the cohesive strength to the point where the paste becomes rubbery. Alkalies (e.g., sodium carbonate) may be added to reduce the viscosity and to increase the penetrating power of the adhesive by acting on the rosin size in the board. Special non-ionic surface-active agents (e.g., Vanesta) may be added to inhibit gelling tendency; these are particularly effective with thin boiling (acid-hydrolyzed) and enzyme-converted starches in which 0.25 to 1.00% of surface-active agent will prevent thickening on standing. Preservatives, defoamers, and plasticizers may also be present. Ordinarily, these materials are added by the adhesive manufacturer, but if enzyme conversion is used, these materials must be added by the user after converting the starch. Dextrins used for making adhesives vary widely in viscosity, color, and adhesive strength. In general, tapioca dextrins are better than corn starch dextrins because of the greater natural tack of tapioca starch. However, the addition of borax to corn starch dextrins makes them comparable to tapioca in tackiness.

The viscosity of the starch or dextrin is extremely important because it determines the solids content at which the paste can be prepared. Starch and dextrin products are available in a wide range of conversion. If the adhesive must set rapidly (as in carton sealing on high-speed packaging machines), concentrations up to 50% solids may be desirable. The dextrin must not be too highly converted, however, since this means that it will produce a relatively weak, brittle film. As a rule, the conventional white and canary dextrins are suitable for carton sealing because they combine quick setting properties with adequate film strength.

Starch Adhesives for Solid Fiber Combining and Sheet Lining. One of the large uses for starch adhesives is in the lamination of solid fiber board. In this process, two or more plies of heavy kraft paper or chipboard (which ordinarily run from 0.009 to 0.030 inches in caliper) are laminated into a thick board suitable for fabrication into boxes or shipping cases.

Sheet lining is similar to solid fiber laminating. In this process, a lightweight sheet of paper such as bond, kraft, coated paper, or glassine is pasted to one or both surfaces of heavy paperboard. In general, the same type of starch adhesive and the same equipment are used for both sheet lining and solid fiber laminating.

Several different methods are used to apply paste in solid fiber laminating. The oldest method, but one which is still used in many places, is to apply the paste between two sheets just before entering the press section, or, in other words, by flooding the nip. In this method, the excess paste is removed by the pressure exerted on the sheet at the press section. Since the pressure exerted at the press rolls also affects the amount of paste forced into the paper, this method of application is lacking in control. To overcome this difficulty, the newer machines use separate glue stations for each glue line applied; each station is equipped with a set of glue rolls which applies a film of paste of predetermined thickness. The pressure exerted on the laminated paper is then regulated independently at the press section.

The conventional canary dextrins are not suited for laminating paperboard because of their low strength and hygroscopicity. The dextrins used for solid fiber laminating are modified to an intermediate degree so that they produce a paste of the desired viscosity when cooked at about 25 to 40% solids. The type of adhesive and concentration at which the adhesive is used depends upon the type of board to be laminated, the type of laminating machine, and the temperature of the paste. The adhesive generally contains from 10 to 20% borax on the weight of the starch. Wetting agents and alkalies are sometimes added to help in the wetting of highly sized papers. On the other hand, if the paper is too porous, the addition of clay or bentonite to the adhesive may be beneficial in reducing penetration.

Ordinarily, starch adhesives are cooked and cooled in the usual manner of cooking starches. As a starting point, the directions supplied by the manufacturer should be followed, but it is frequently necessary to make slight adjustments in order to satisfy local conditions. The cooking tank should be equipped with a direct steam line, since some starches are so highly modified that they tend to "burn" on steam coils. Coils in the tank are useful, however, for cooling the paste and for controlling the temperature of the paste. It is best to withhold part of the water during cooking and then to add as much as necessary of the remaining water after cooking to obtain the desired concentration and viscosity.

The paste is ordinarily applied at or near room temperature (85–120° F.). However, there has been a trend in recent years, when laminating highly sized kraft and chipboard, to use the paste at high temperatures (160–180° F.) in order to obtain the maximum tack and to obtain rapid setting of the paste through cooling when it contacts the relatively cool paper. By using higher temperatures, it has been possible to obtain increased production and to decrease the consumption of adhesive.

It is desirable to use a paste of the lowest possible solids compatible with the production of the driest and most rigid board. However, the solids must not be so low that excessive moisture is added to the paper, since this causes curling and leads to shrinkage. Shrinkage after the laminated board has been cut to a definite sheet size is very undesirable. For example, if laminated paperboard is cut to the dimensions of a standard box, excessive shrinkage will reduce the dimensions and result in a box which is too small. The two most important factors in determining the amount of moisture added to the board are the thickness of the glue film and the solids content of the glue. Pastes of high solids produce board of lower moisture content than pastes of low solids, provided a glue film of the same thickness is applied in both cases. For this reason, pastes with solids content as high as 30 to 50% are used when board of very low moisture content is desired. However, pastes as low as 20% solids can be used to produce board of low moisture content by applying thin glue films.

TABLE I

EFFECT OF PASTE CONCENTRATION ON CONSUMPTION OF ADHESIVE

Per cent solids in starch paste	Pounds of dry starch used per 1,000 sq.ft. of glue line
20	2.1–2.3
25	2.5–2.75
30	3.0–3.2
35	3.5–3.7
40	4.0–4.2
45	4.5–4.7
50	4.8–5.2

The consumption of adhesive is important for its effect on the amount of moisture added to the board and for its effect on the cost of laminating. The amount of glue consumption is dependent primarily upon the thickness of the glue line and the concentration of the adhesive. Table I shows the effect of concentration on consumption of adhesive when well-sized chipboard or kraft papers are used. The consumption will be slightly higher for slack-sized papers.

The consumption of glue varies with the number of glue lines in the laminated product which, in turn, depends upon the number of plies and the type of laminating machine. If the laminating machine is of the type which has multiple glue stations (i.e., a glue applicator box for each glue film) and the glue is applied to only one surface, the number of glue lines will always be one less than the number of plies. On the other hand, if the machine is of the older type, in which the glue is fed between the two plies, the number of glue lines is determined as follows:

Number of plies	Number of glue lines
2	1
3	2
4	4
5	6
6	8

Water-Resistant Starch Adhesives for Solid-Fiber Combining. Water-resistant starch glues are becoming increasingly important for solid-fiber combining and for pasting multiwall paper bags. In this process, the starch is used in combination with water-soluble urea-formaldehyde condensates to produce a film which is insoluble in water and has a high degree of wet strength. Laminated products can be obtained which show no paper-fiber failure even after a week of soaking in water.

Starches vary considerably in their reactivity with urea-formaldehyde resins. Starches with high gelling tendency are the most reactive, due to their higher molecular weight. Figure XX-1 shows the results obtained with several different types of starch when prepared with different amounts of urea-formaldehyde resin on the basis of the starch. The vertical ordinate shows the per cent delamination which occurred when the laminated board was soaked for twenty-four hours in water at 80° F. As can be seen, there is considerable difference in the water resistance of the bond, depending upon the type of starch used. The acid-hydrolyzed starch and the high-viscosity dextrin produced the greatest water-resistance with the smallest amount of resin.

In general, 8 to 25% urea-formaldehyde resin, based on the weight of the starch, is used. The resin is usually added to the starch paste after cooking, although in some cases, the two may be cooked together under carefully controlled conditions. The mixture must be catalyzed with an acid catalyst, and usually alum or ammonium chloride is used. No reaction will take place under alkaline conditions, and consequently the usual borated starch adhesives cannot be used. A formula is (see also p. 1227):

Step 1. Cook the starch at the proper concentration, which is usually between 20 to 25% solids. (This should be a special starch containing no alkali.) Cool the paste to room temperature.

Step 2. Add sufficient urea-formaldehyde resin to give 8 to 25% resin on the basis of the starch. This may be commercial resin syrup or a syrup made by dissolving dry resin in a small amount of water. Adjust the *p*H to about 6.0.

Step 3. Add 1 to 1.5% of ammonium chloride based on the total weight of paste, i.e., starch, resin, and water.

The above paste will not be as tacky as regular starch adhesive because it contains no borax, and as a result, the laminating machine will have to be run at a slightly lower speed.

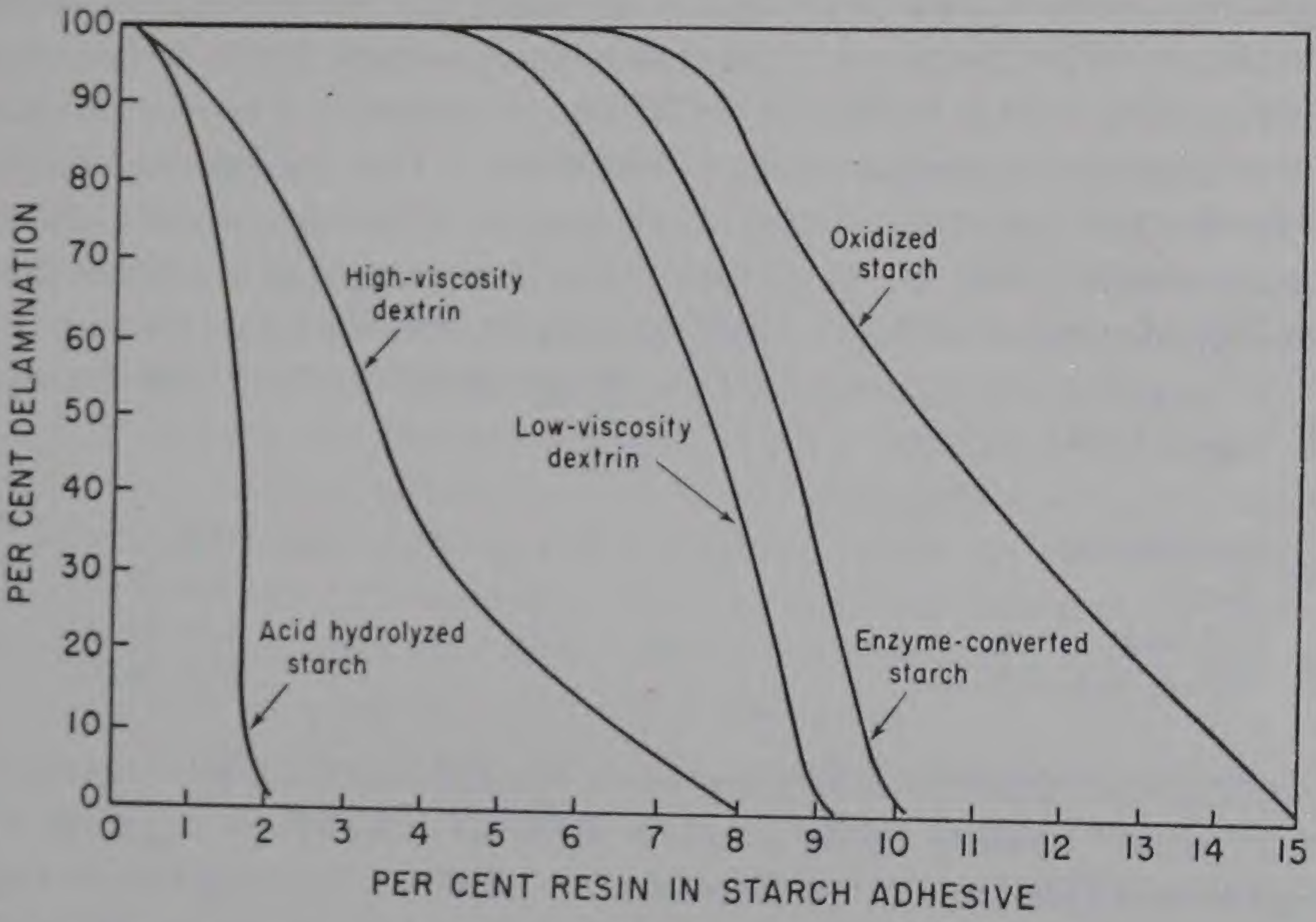

Fig. XX-1. Effect of urea-formaldehyde resin on the water resistance of starch adhesives.

After the paper is combined, heat should be applied to speed up the reaction between the resin and starch. Unless a high temperature is applied, the reaction is rather slow, and the laminated product will have to be aged for several days before maximum water resistance is developed. Aging should always be carried out in a warm room, because it has been found that aging in a cold warehouse is not satisfactory and actually may prevent the final development of water resistance.

The paper used with urea-formaldehyde resin-starch glues should be dense and highly sized with rosin. If the paper is made from kraft, the pulp should be well washed and treated with sufficient alum to prevent any eventual bleed of alkali from the fibers into the glue line.

Starch Adhesives for Corrugated Board. Corrugated board manufacture is an important part of the paperboard industry. The familiar corrugated shipping case is to be seen everywhere and promises to become increasingly popular because of its durability, light weight, and other good properties.

Regular corrugated board is made with one corrugating medium and two liners. Another combination sometimes used consists of one corrugating member and one liner, which is known as single-lined board. If two corrugating members and three liners are used, the board is called double-double board. The liners are made from heavy-weight kraft or jute paper and are usually 0.012, 0.016, or 0.030 in. in caliper. The liners should have the qualities of toughness and durability. The corrugating medium is made of straw, chestnut, kraft, waste paper, or semichemical pulp, and is usually about 0.009 in. in caliper. Good corrugating medium should have a high degree of stiffness, uniform caliper, and uniform moisture content. Nine-point corrugating medium is generally made in the following weights per 1,000 sq.ft.:

Strawboard	34 lb.
Kraft	24 to 26 lb.
Chestnut	32 to 34 lb.
Waste paper stock	26 to 28 lb.

Corrugated board is fabricated on a special machine, the corrugating machine, which consists in its simplest form of a set of corrugating rolls, glue applicator rolls, and a hot plate section. Before entering the corrugating rolls, the corrugating medium is preconditioned by steaming and is then further heated at the steam-heated corrugating rolls. This treatment with moist heat makes the paper soft and pliable so that uniform corrugations are produced, and prevents sticking of the paper to the corrugating rolls. The number of corrugations per foot of board and the height of the corrugations are standardized as follows:

Type of flute	Height of flutes, in.	Number of flutes per foot
A	—	36
B	1/8	51
C	5/32	41

A flute is used where high top-to-bottom compression and where maximum cushioning is desired, e.g., for board used in the packaging of paper cartons and glass jars. *B* flute is used where high end-to-end compression is desired; it is used for the packing of canned goods and where the box is stitched instead of being taped.

On leaving the corrugating rolls, the corrugated medium fluffs out to meet a glue applicator roll which applies adhesive to one side of the paper. Long metal strips (fingers) are set to control the amount of this fluffing out, and the setting of these fingers is one of the most important parts of the operation of a corrugating machine, since the improper setting causes damaged flutes and poor adhesive application. Immediately after the application of glue, the first liner is brought into contact with the glued side of the corrugating medium, and then (on pressure type machines) high pressure is applied for a fraction of a second to set the adhesive. The resulting board, now known as single face, then passes to the double-back glue station where adhesive is applied to the flutes on the other side of the corrugating medium and a second liner applied. Only a slight amount of pressure can be applied at this point (because of danger of crushing the corrugations), and consequently, adhesion is more of a problem than it is for the single face. If the flutes are uneven, only the high flutes will receive glue and the adhesion will be spotty.

After leaving the double-back glue station, the combined board enters the hot plate section where the board is held against heated platens by means of heavy belts. Setting of the adhesive on the double-back side takes place at this point. At the end of the machine, the board is slit and flap-scored. The blanks are then taken off the machine and piled in such a way as to minimize warping and sweating of the board.

The wet glue bond must be fairly strong as the board comes off the machine to withstand the handling at this point. Later, the adhesive sets to produce the final dry bond. This bond makes an important contribution to the over-all strength of the finished board, affecting such properties as bending moment, column compression, tensile strength, puncture resistance, and water resistance.[16] Improperly applied adhesive resulting in starved or flooded joints and poorly made corrugations, masked flutes, and deep finger lines reduce the strength of the bond.[17]

Some of the tests used to measure the properties of the finished board are mullen, puncture, crush, impact, score tear, adhesion, compression, drop, and drum test, the last four tests being made after the board has been fabricated into a box. End-to-end and top-to-bottom compression tests on the sealed but empty case are widely used as a quality control standard. Either maximum compression or compression at ¾ in. deflection can be used. The crush test is widely used on the board before fabrication into a box; good *C* flute board will pass a crush test of 35 to 50 p.s.i., *B* flute board being somewhat higher, and *A* flute board being somewhat lower.

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[16] R. E. Green, R. H. Sams and J. H. Wills, *Fibre Containers* 49–52 (Oct., 1947)

[17] R. E. Green, R. H. Sams and J. H. Wills, *Paper Trade J. 125*, No. 4: 45–48 (July 24, 1947)

The two principal adhesives used in corrugating are starch and sodium silicate. Asphalt is used in a small number of cases for making a special water-resistant board. Starch- and silicate-combined board can be distinguished from each other by adding a few drops of phenophthalein solution and iodine solution to the glue line. Iodine will stain starch blue, whereas phenophthalein produces a strong red color with silicate, but not with the starch.

The conventional starch or dextrin glues used in solid fiber laminating are not suitable for making corrugated board because of the slow setting rate of these adhesives. Furthermore, these adhesives contain so much water that they wet the corrugated medium to an excessive degree and produce soggy board. To overcome these objections, a special process has been developed for making corrugated board.[18-20] This process involves the use of a two-component starch adhesive consisting of ungelatinized (uncooked) starch suspended in an aqueous solution of gelatinized (cooked) starch of sufficient viscosity to keep the ungelatinized starch granules in suspension. The paste ordinarily contains a ratio of four parts uncooked starch to one part cooked starch, and a total solids content of about 20%. The theory of this unique paste is that (when the paste is applied to the tips of the corrugations in the usual manner and the board is passed through the hot plates) the heat in the hot plates will gelatinize the uncooked starch in the paste, resulting in a tremendous increase in the viscosity and tack of the glue film. This rapid increase in viscosity brought about by heating of the glue film produces a wet bond sufficiently strong to hold the board together while it is cut into sheets at the end of the machine. Heat is absolutely essential in order to gelatinize the uncooked starch in the paste, and the starch film must reach a temperature of at least 140 to 150° F. This is an important difference between this adhesive and silicate, inasmuch as silicate-combined board will set up in the stacks even though the wet bond is weak on the board coming off the machine. With starch paste, however, practically no bond will be formed if there is too little heat on the hot plate section of the machine. Insufficient heat is indicated by a very weak bond and a glue line which has a white granular appearance caused by the presence of ungelatinized starch.

The preparation of the above starch adhesive must be carried out in the corrugating plant under the direction of a man who has been especially trained for the job. A number of different ingredients are used. Un-

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[18] J. V. Bauer, U. S. 2,051,025 (Aug. 12, 1936)
[19] J. V. Bauer, U. S. 2,102,937 (Dec. 21, 1937)
[20] J. V. Bauer, U. S. 2,212,557 (Aug. 27, 1940)

modified (pearl) starch is used as the ungelatinized (uncooked) starch component because it gives the greatest increase in viscosity on heating. Borax is added to increase the viscosity developed by the uncooked starch on heating. Sodium hydroxide is added to lower the gelatinization temperature of the uncooked starch, so that the starch will be readily gelatinized in the hot plate section of the corrugating machine. Enough sodium hydroxide should be used to lower the gelatinization temperature of the starch to 140° F. For the carrier or gelatinized starch portion, a partially modified starch is generally used, and this is gelatinized with heat or with sodium hydroxide. The principal function of this carrier is to prevent the settling of the raw starch granules and to keep the adhesive mixture from soaking too rapidly into the paper.

A formula for starch adhesive suitable for domestic corrugated board is given below. This grade of board is generally made with two liners of well-sized kraft and a corrugating medium of unsized chestnut, straw, kraft, or semichemical.

No. 1 portion (carrier or gelatinized portion)	448 lb. cold water 117 lb. slightly modified starch 16 lb. sodium hydroxide in 30 lb. water
No. 2 portion (uncooked starch portion)	1520 lb. cold water 16½ lb. borax 468 lb. dry unmodified starch

A wetting agent, such as sulfonated castor oil (about 3 pints), is sometimes added if the paste is to be used with highly sized kraft liners. A preservative such as formaldehyde is also added.

The No. 1 and No. 2 portions are prepared separately. The No. 1 portion, which is highly viscous or gummy, is added to the No. 2 portion, which consists of a thin slurry of starch in water. After mixing the two components vigorously for fifteen to twenty minutes, the paste is ready for use. The paste is thixotropic and tends to thicken on standing, and consequently must be agitated continuously to break down the false body. Accurate control of the viscosity is essential. The consumption of paste is approximately 12 lb. of liquid paste per 1,000 sq.ft. of double-face board (two glue lines).

Water-resistant starch adhesive suitable for corrugating can be prepared by using urea-formaldehyde resin in combination with starch. In preparing this paste, the starch in the carrier portion (No. 1 portion) is not gelatinized with sodium hydroxide, but rather it is gelatinized with heat. A satisfactory formula is given:

No. 1 portion (carrier or gelatinized portion) ..	117 lb. slightly modified starch 832 lb. water 1¼ lb. sodium hydroxide (optional) (Cook with live steam to 190° F.)

No. 2 portion (ungelatinized portion)	585 lb. unmodified starch 1100 lb. water 52 lb. alum

(Mix for 15 minutes)

After preparing each portion separately, the No. 1 portion is added to the No. 2 portion. Then, after cooling to 80 to 85° F., 105 lb. dry urea-formaldehyde resin dissolved in 150 lb. water is added. The paste is finally mixed, and the *p*H is checked and adjusted to 4.0 to 4.5. If regular alkaline starch paste or silicate has been used in the system previously, the pipelines in the paste system should be thoroughly cleaned with water containing a small amount of alum, so that all residual alkali in the system will be neutralized.

The above is known as weatherproof paste, since it produces a board which is resistant to water. The board, which is generally made from two highly sized kraft liners and a highly sized kraft corrugating medium, is used mostly for overseas shipping cases and for domestic cases where the box must stand up under conditions of high moisture content. Properly made weatherproof board can withstand at least twenty-four hours' immersion in water without delamination. The consumption of this paste is higher than that of regular paste, being in the neighborhood of 20 to 22 lb. of liquid paste per 1,000 sq.ft. of double-face board (two glue lines).

Within very recent times, experiments have been carried out on the use of water-soluble ketone-aldehyde resins for making water-resistant corrugating paste with starch. It has been claimed that 5% of this resin based on the starch will produce a water-resistant bond. Heating to 140° F. is required to cure the resin-starch bond, and resorcinol to the extent of 5% on the weight of the resin is helpful in some cases in developing a rapid cure. These resins are interesting because they can be cured at *p*H values between 10 to 11 and hence can be used in regular alkaline paste.

Starch Adhesives for Bag Pasting. Starch adhesives are used for the pasting of kraft grocery bags and also for the pasting of 100-lb. multiwall kraft shipping bags. Several types of starch adhesive are used, depending upon the type of equipment and whether the paste is used on the seams or on the bottoms of the bags. One important requirement for all bag pasting adhesives is that they do not string or throw when applied by the disk applicator, since this spots the bags with glue.

On a Potdevin, or similar bag machine, where the complete grocery bag is made in one operation, the seam paste must be rapid setting so that the seam will not slip or move when the bottom of the bag is pasted a few seconds later. This means that a high-solids borated dextrin is required for pasting the seams.

Generally speaking, the same type of seam paste is used for both kraft grocery bags and multiwall kraft shipping bags. This same paste is also used for holding together the plies in a multiwall bag (where the glue is applied in spots to hold the various plies together). A typical seam paste is:

90 lb. converted dextrin
10 lb. borax
0.5 lb. sodium hydroxide
30 gal. water

Bottom pastes do not have to be fast setting, since the adhesive has a chance to set while the bags are being stacked. Consequently, low-solids pastes are used for pasting the bottoms. Unmodified (pearl) starch is often used, and in some cases special starches thicker than pearl starch are used for this purpose. These lower the pasting costs because of the low solids at which they are used, and the lard-like consistency of this type of paste makes it easy to squeeze the paste into the corners and folds. On bag machines which paste the seams and bottoms in two separate operations, it is possible to use the bottom paste for both operations. A typical bottom paste is:

100 lb. thick-boiling starch
75–80 gal. water
0.5 lb. soap
0.5 lb. sodium hydroxide

The addition of sodium hydroxide to the seam and bottom paste is desirable only if highly sized and dense paper is used. If the paper is weakly sized and has a low density, it is desirable to leave out the sodium hydroxide and, in extreme cases, to add an anti-penetrating agent such as bentonite or vegetable gum. The paste should be as rapid-setting as possible in order to minimize penetration and prevent staining of the outside of the bag.

Water-resistant adhesives are required for pasting the seams and bottoms of multiwall bags used for packing potatoes and chemicals. Starch-urea formaldehyde resin glues have proved satisfactory for this purpose (see pages 1220–1222). A formula is given below:

100 parts special dextrinized starch (or a mixture of thin-boiling starch and dextrin)
8–10 parts powdered urea-formaldehyde resin
2–3 parts ammonium chloride

In this case, all the ingredients may be heated together to a temperature of 195 to 200° F. for fifteen to twenty minutes and then cooled to room temperature. This paste forms a highly water-resistant glue line within a period of three to four days after the bags are pasted. The paste has a tendency to thicken on standing. Hill and Sliwinski[21] recommend the addition of 5% sodium chloride and 1% hydrogenated vegetable fat for increasing the pot life.

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[21] E. H. Hill and V. X. Sliwinski, *Tappi 32,* No. 7: 297–299 (July, 1949)

Starch Adhesives for Pasting Bristols. Unmodified starch is used for pasting wedding bristols, announcement cards, menus, etc. In this process, the starch (pearl) is cooked at high concentration to produce a solid gel, which is then applied to the paper in excess. The paste is fed to the paste rolls in large chunks or fed to a grinder which disintegrates the paste before pumping it to the paste rolls. The paper is run between press rolls to squeeze out the excess paste, after which the laminated sheet is run over driers.

Unmodified or thick-boiling starches are used because they produce maximum stiffness and keep the costs low. The pasted sheets are generally plated to produce either a vellum or antique finish. One of the important final requirements is a high degree of snap, which can be judged by flexing one corner of the sheet to test the speed of recovery.

Starch Adhesive for Tube Winding and Carton Sealing. Prepared starch adhesives are used for making paper tubes and paper cans. In making these products, glue is applied to a strip of paper which is then wound, either in a spiral or a straight winding, into a tube. The tube is then cut to size on leaving the mandrel. Borated dextrin-type adhesives ranging in solids from 33 to 70% are used for this purpose. A fast-setting rate is one of the requirements. Mixed animal glue and dextrin adhesives are sometimes used, i.e., when the label is stuck to the tube with the same paste used for making the tube.

Considerable quantities of dextrin adhesives are used for case sealing and carton sealing. Usually these glues are sold by the adhesive manufacturer in liquid form. A large number of products is available. Fast setting is the most important requirement, since the machines are operated at very high speed.

Sodium Silicate

Sodium silicate is widely used as an adhesive for the combining of corrugated paperboard and for the lamination of solid fiber board. It is also used for laminating aluminum foil to paper. Sodium silicate is a relatively inexpensive material and is sold in tanks cars in ready-to-use form.

When selecting silicate, there are several factors which must be considered, among the most important of which is the ratio of SiO_2 to Na_2O, since the ratio of these two ingredients affects the viscosity, gelation characteristics, and specific adhesion of the silicate. Silicate is available commercially ranging from $2Na_2O \cdot 1SiO_2$ to $Na_2O \cdot 4.0SiO_2$. Silicates having a ratio of about 1 to 2.8 (soda to silica) have the greatest cohesive strength, whereas silicates having a ratio of above 1 to 3.5 (soda to silica) have the lowest cohesive strength (in the wet state), but have the highest setting rate.

At ratios of silica to sodium of over 4.2 to 1, the solution is unstable and tends to form a jelly-like semi-solid through slight evaporation of water. The most common silicate for laminating is $Na_2O \cdot 3.3SiO_2$, which is generally sold in liquid form at 42° Bé. (approximately 39% total solids). The sodium oxide (Na_2O) content is determined by titrating the silicate (after dissolving in hot water) with 0.2 *N* hydrochloric acid, using methyl orange as the indicator. The silica content (SiO_2) is determined by adding additional acid after titration in several treatments with intermediate evaporations and finally digesting on a steam bath. The silica is determined after ignition by weighing the residue.

All solutions of silicate above the ratio of $Na_2O \cdot 1.5SiO_2$ can be concentrated to viscous liquids. The solutions are truly viscous, but as the solution is concentrated (as in the drying of adhesive films), the viscosity increases greatly and the solution changes from a fluid to a tough, plastic mass. If silicate is reacted with acids, a gel of high mechanical strength and rigidity is obtained. The gel is irreversible and cannot be redispersed by neutralization of the acid.

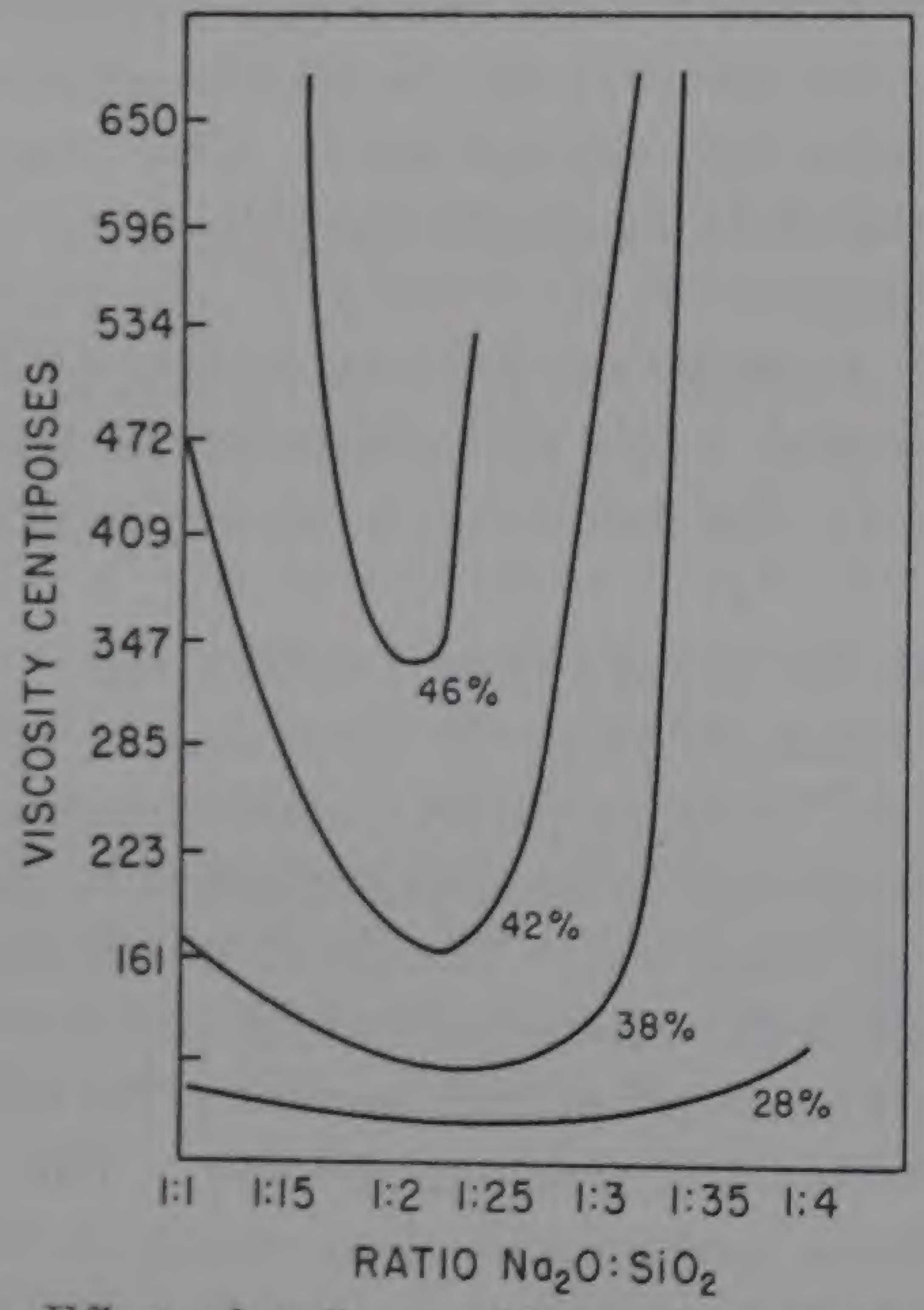

Fig. XX-2. Effect of sodium oxide to silica ratio on the viscosity of silicate solutions of different concentrations.

The highly siliceous silicates (i.e., those with high ratios of silica to sodium oxide) show the most striking viscosity change for small changes in concentration. This is shown in Figure XX-2,[22] where the effect of sodium oxide to silica ratio on viscosity is plotted at several different concentrations. The high-silica silicates not only tend to increase in viscosity more rapidly, but also produce more elastic gels. The viscosity is greatly affected by temperature, particularly in the case of the highly siliceous (least alkaline) grades. The viscosity temperature relationship is practically a straight-line one, the slope increasing as the ratio of silica is increased. At high concentrations silicate acts almost as a thermoplastic material.[23]

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[22] J. G. Vail, *Soluble Silicates in Industry,* The Chemical Catalog Company, New York, N. Y. (1928)

Clays are sometimes added to sodium silicate to increase the thixotropic properties and increase the setting rate. The addition of clay increases the solids content and thus reduces the amount of water which must be evaporated to set the adhesive. On the other hand, the addition of clay makes it possible to use a more dilute liquid phase which improves the wetting properties of the adhesive for the highly calendered and hard-sized papers which have come into general use.[24] Clay also acts to control the penetration of adhesive into the paper by helping to contain the residual silicate in the glue line.

Dilute solutions of silicate freeze fairly readily, in which case the crystals appear on the surface while the silicate at the bottom becomes more concentrated. Thawing and remixing, however, return the silicate to its original state.

Use of Silicate in Solid-Fiber Laminating. Silicate produces a strong, hard, elastic bond, although the bond may be brittle if the glue line is too thin or overdried. Silicate yields a water-resistant film, but the high alkalinity destroys the sizing on the fibers adjacent to the glue film, thereby causing them to let go when wet. The alkali in silicate has a tendency to migrate into the board under conditions of high moisture, and in some cases where the board has been stored at high humidity, the alkali has been known to migrate to the surface and produce staining. This alkali destroys the size, discolors the fibers, and attacks alkali-sensitive inks and dyes. It is generally believed that this diffusion is a sort of hydrolysis which leaves most of the silica in place and permits the sodium to diffuse to the surface of the board.[22] Coating the outside liners of the board with reactive chemicals overcomes the troubles with staining.[25] Precoating of the paper with aluminum chloride before laminating is said to increase the water resistance of the combined board.[26]

The consumption of silicate in solid-fiber laminating is generally about 6 to 8 lb. of solid silicate or, in other words, about 18 to 20 lb. of liquid silicate per thousand square feet of glue line. This adds more weight to the board than is the case with most adhesives and is, in general, an advantage, since weight is a factor in pricing the board. The silicate also adds considerable stiffness to the board. The maximum adhesive strength in fiber board laminated with silicate is apparently not obtained until about four hours after lamination.[27]

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[23] E. R. Boller, J. G. Lander and R. Morehouse, *Paper Trade J. 110*, No. 12: 167–176 (Mar. 21, 1940)

[24] J. H. Wills, *Paper Trade J. 127*, No. 2: 304–307 (July 8, 1948)

[25] J. D. Carter, U. S. 2,015,359 (Sept. 24, 1935)

[26] J. D. Carter, U. S. 2,414,360 (Jan. 14, 1947)

Use of Silicate in Corrugating. Until recent times, silicate was about the only adhesive used for making corrugated paperboard. It is still widely used although it has been replaced in some cases by starch (see previous section). Silicate has the advantages of high solids content, rapid setting rate, and strong adhesive qualities.

The decided increase in viscosity which silicate undergoes upon losing only a small amount of water accounts for the fast setting rate. The quick set of silicate adhesives with small water loss is also a factor in preventing softening of the paper. The finished product has, therefore, a smooth surface and the flutes maintain the round tip formation which results in maximum strength and caliper. The operating performance of silicate is largely determined by the water loss required for initial set, since this determines the maximum operating speed.[28] The water loss required for set varies from about 1.35 to 1.50 lb. of water per 10 lb. of silicate.[29, 30] In some cases, a low viscosity silicate is used on the single facer and a high viscosity silicate is used on the double backer. Silicate-clay mixtures are sometimes used where exceptionally fast setting is desired.

One objection to the use of silicate for corrugating is that it forms hard, glassy deposits on the machine. However, there are additives which the manufacturer recommends to lessen this problem. An advantage of silicate is the high compression strength of the combined board resulting from the presence of shoulders of dried silicate between the corrugating medium and the liner. Enough glue should be applied to produce these reinforcing shoulders.

The consumption of silicate in corrugating runs from 18 to 23 lb. of liquid silicate per thousand square feet of double-faced board, depending upon the type of paper used. The size of the flute is also a factor; for example, when 18 lb. of silicate are consumed for *A* flute board, a comparable consumption for *B* flute board would be 22 lb. The desired degree of penetration of silicate into the liner is no more than 0.002 in.[31]

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[27] H. M. Hale, *Second Progress Report, Project L-207-4,* Forest Products Laboratory, Madison, Wisconsin (Mar. 11, 1919)

[28] J. H. Wills and R. H. Sams, *Ind. Eng. Chem. 41:* 81–86 (1949)

[29] F. W. Padgett and R. B. Killingsworth, *Paper Trade J. 122,* No. 19: 201–207 (May 9, 1946)

[30] R. L. Kreyling, *Tappi 32,* No. 5: 238–240 (May, 1949)

[31] E. R. Boller, J. G. Lander and R. Morehouse, *Paper Trade J. 110* No. 12: 167–176 (Mar. 21, 1940)

Protein Adhesives

At one time proteins were the most important adhesive material used in the paper industry. Today, this is no longer true because protein adhesives have been replaced to a considerable extent by cheaper materials such as starch, dextrin, and sodium silicate adhesives. Casein, animal glue, albumen, soluble dried blood, and soybean protein are now rarely used except for specialty papers.

Protein glues have some very definite advantages over other adhesives. They produce stronger bonds than starch or dextrin glues, which is important for some purposes, although of only minor importance in the lamination of paper products, because nearly all glues are stronger than paper. Protein glues tend to produce more flexible and continuous films than either starch or sodium silicate, which is useful for the lamination of stock for paper cans and bottles where oil resistance is desired. Another advantage is that proteins can be formulated so that they produce highly water-resistant glue lines, but this has become of less importance since the recent development of the starch-urea formaldehyde glues. Some of the more important protein glues are discussed in the following sections.

Casein Glues. Casein dispersed in alkali makes a strong adhesive. The most important alkali used for dispersion is sodium hydroxide, although lime is frequently added when water resistance is desired. An example of a water-resistant casein glue suitable for gluing wood veneers is given below:

Casein	100 parts
Water	200–230 parts
Hydrated lime	20–30 parts
Water	100 parts
Sodium silicate	70 parts

Casein adhesives can be rendered highly water-resistant by treatment with a tanning agent. The agent can be mixed into the adhesive, if care is taken to prevent coagulation. Under these circumstances, water resistance develops gradually upon drying of the adhesive film. Formaldehyde, paraformaldehyde, and copper salts are some of the materials which can be added to casein glue to increase the water resistance. Rubber latex, urea-formaldehyde resins, and other similar materials may be added to casein glues.

Soybean Glues. Soybean protein can be used in the same way as casein. For some purposes, soybean protein is preferred because of its lower viscosity and greater tolerance for formaldehyde.

Soy flour is used to some extent in the adhesives industry, but mainly as a filler, since it has very little tack of its own. Usually the flour is dispersed in sodium hydroxide, and for special purposes, a little carbon disulfide may be added.

Blood Glues. Soluble dried blood obtained from the meat packing industry can be used as an adhesive after dispersing in water with ammonia. Blood glues are heat gelling and can be readily converted into a water-resistant form by heat alone. Blood glues have been used in plywood manufacture where a water-resistant bond is desired. Recently, however, blood glues have been replaced to a large extent by the urea- and melamine-formaldehyde resin glues.

Animal Glues. Animal glue is a protein adhesive which is still being used to a large extent in the paper industry. In preparing animal glue for adhesive purposes, the dry glue (in either ground or flake form) should be stirred into cold water and allowed to soak for several hours. After soaking, the glue should be melted by heating in a water- or steam-jacketed tank to a temperature of 50 to 60° C. High temperatures and long heating should be avoided. Ordinarily, about 2 to 4 parts of water are used for each part of glue, depending on the jelly test of the glue.

One of the large uses of animal glue is for the production of gummed papers, which is described in a later section. Animal glues are also used to a large extent as bookbinding adhesives, for folding and set-up boxes, for tube winding and cans, and envelopes. A typical bookbinding adhesive can be made from 25% glue, 25% glycerin, and 50% water, together with a small amount of preservative and terpineol for masking the odor of the glue.

For making water-resistant glues using animal protein, a small amount of formaldehyde, hexamethylenetetramine, or paraformaldehyde should be added. About 1 to 5% formaldehyde on the dry weight of the glue is ordinarily used. Urea, calcium nitrate, glycerine, sorbitol, or similar compounds are sometimes added to animal glues to plasticize the glue film and improve the remoistening properties.

Fish Glues. Fish glues, which are derived from the heads, skins, and other parts of fish, were once widely used. These glues are now used very seldom, although they find some use in photoengraving and in the manufacture of gummed labels.

Other Aqueous Adhesives

There are many other water-soluble materials which can be used for adhesive purposes. Among these are the water-soluble cellulose derivatives, polyvinyl alcohol, vegetable gums, cereal flours, and water-soluble synthetic resins.

Polyvinyl alcohol makes a very desirable adhesive for some purposes. The paste is non-tacky, but a strong bond is produced on drying. The film is highly resistant to water and requires no heating or curing period. The commercial product contains a high percentage (50%) of clay which reduces the cost. Good results can be obtained with thin films, which helps to further reduce the cost. Polyvinyl alcohol can be mixed with starch, but the starch must not contain borax, alum, or formaldehyde since these materials cause gelling. Polyvinyl alcohol is incompatible with sodium silicate.

Among the vegetable gums, gum arabic is the most widely used adhesive. This material can be dissolved in 2 to 3 times its weight of water to produce a strong adhesive. Gum arabic is used as a remoistening adhesive on cigarette papers. However, the high cost of gum arabic in comparison with other adhesives limits its use.

Gummed Papers and Paper Tapes

Gummed papers are widely used for the manufacture of stamps, seals, labels, sealing tapes, presized wallpaper, mending tapes, etc. Gummed papers and paper tapes have a surface coating of water-soluble adhesive which is remoistened with water just before use to produce a tacky quick-setting adhesive. Other special types of gummed paper contain a coating of water-insoluble adhesive which can be activated by organic solvents, by heat, or by pressure.

Gummed papers are made on a gumming machine which consists of a fountain roll, an applicator roll, and a pressure roll. The thickness of the adhesive film applied to the paper is determined by the pressure between the applicator and pressure rolls. The adhesive is generally applied hot. After coating, the sheet is passed through a drier which may be the festoon type or the tunnel type. In the tunnel type, tension on the sheet prevents curling, whereas in the festoon drier, curling is held to a minimum by careful control of the humidity and temperature. The adhesive film should never be dried below a moisture content of 4.5%. After drying, the paper can be passed over a breaking machine to crack and break the gummed layer. The film is generally broken in two directions by passing it over the breaking bar twice. This reduces the tendency toward curl, but even so curl is a problem with gummed papers. Animal glue, dextrin, casein, fish glue, and gum arabic are some of the adhesives used in making gummed paper. Animal glue and dextrin are the most important. About 6 to 10 lb. of adhesive is generally applied (17 × 22—500).

Remoistening Gums. Highly converted dextrins are used for postage stamps, envelope gums, and paper labels. Tapioca and potato dextrins are preferred. Ordinary corn dextrins are considered inferior, but excellent dextrins can be produced from the waxy varieties of corn. The requirements for a good dextrin are low viscosity, high solubility, low reducing sugar content, fast drying rate, and high film gloss. Low reducing sugar content is desirable in order to prevent discoloration due to the reaction of the sugar with the degraded protein-like products in the paper. Fast drying is desirable because it permits rapid machine operation. The glue should not string or cotton, since this interferes with the operation of the machine.

A high percentage of plasticizer (glycerine, corn syrup, etc.) is generally used to reduce curling and brittleness and to improve the remoistening properties. Too much plasticizer must not be used, however, as this causes blocking of the film. Urea is very effective as a plasticizer when used in high percentages.[32] Wetting agents such as sulfonated castor oil are added, and sometimes oil of wintergreen or other essential oils are used for flavoring. Borax can be used to improve the tackiness. Preservatives may be added in some cases.

Stamps and labels are made of sulfite paper, usually in a basis weight of 50 to 60 lb. Paper lighter than this is likely to result in strike through of the adhesive, whereas heavier paper is expensive and likely to be hard to paste. In general, labels for bottles are cut so that the machine direction is horizontal. The paper should be fairly well sized in order to prevent excessive penetration of the glue. A smooth surface is important where the paper is to be printed.

Sealing Tapes. The requirements of an adhesive for sealing tape are many. The glue film must be non-blocking, but must be capable of absorbing water evenly. The film must be tacky and quick setting when moistened. However, the film must not set too rapidly, since a certain amount of slip is desirable in order that the tape may be moved slightly after it is put in place. The film must be thick enough so that it will be softened no more than one-half of its thickness, regardless of how much water is used for moistening.[33] On the other hand, the film must not be so thin that there will be inadequate bonding when the tape is applied to porous papers. As a final requirement, the adhesive strength of the glue must be exceptionally high. This last property can be measured on a gummed tape tester which records the force necessary to break the bond produced by the moistened tape.

Animal glues fulfill the above requirements better than starch or dextrin adhesives and hence are most widely used for making strong paper tapes. Generally, a mixture of hide and bone glues is used. Kraft paper is generally used because of its good strength. Three grades of base paper are used: light weight (35 to 40 lb.), medium weight (60 lb.), and heavy weight (90 to 120 lb.). The amount of adhesive varies with the weight of the paper, being about 15 lb. or less for the light-weight grades and 18 lb.

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[32] H. F. Bauer, J. V. Bauer and D. M. Hawley, U. S. 2,144,610, and 2,145,195 (Jan. 24, 1939)

[33] *Fibre Containers* 60–62 (June, 1945)

or more for the heavy-weight grades. The finished tape is usually double-wrapped to protect the glue from excessive moisture.

A special patented grade of sealing tape, called Sisalkraft, is a gummed product consisting of two plies of kraft paper (a 50- and a 30-lb. sheet) laminated with asphalt which is reinforced with sisal fibers. The sisal fibers embedded in the asphalt run either lengthwise or crosswise, depending upon the type of strain which the tape is subjected to in use. About 25 to 30 lb. of animal glue are applied in the gumming operation and the paper is embossed. Special care is required in drying of the glue film to prevent delamination of the asphalt; the drying temperature must be kept below 200° F.

Emulsion Type Adhesives

Emulsion type adhesives have become increasingly important in recent years. Among the most important of the emulsion type adhesives are rubber latex, synthetic rubber latices, synthetic resin emulsions, and asphalt emulsions. In general, emulsion adhesives consist of a resinous base material dispersed in water and a plasticizer. Compounding of the adhesive can be regulated to control the drying rate, flexibility of film, and similar conditions. In some cases, a solvent for the resin is used, particularly when the adhesive is to be used on impervious surfaces (e.g., lacquer-coated papers or on cellulose acetate sheeting).

Emulsion adhesives have many good features. They can be used at very high solids content, which means that their setting rate is high and only a small amount of water is added to the product. Setting is rapid because the emulsion breaks as soon as it contacts the paper surface. Emulsion adhesives can be made to produce water-resistant bonds and, in some cases, water-vapor-resistant bonds. Reduced warp and greater film flexibility are other advantages.

Resin-emulsion adhesives can be made to work where other adhesives are unsatisfactory. Resin-emulsion adhesives combine the desirable features of both aqueous and non-aqueous base adhesives. Thune[34] points out that acetate sheeting can be readily laminated to chipboard with a resin-emulsion adhesive because the water in the emulsion wets the paper at the same time that the organic solvent in the emulsion wets the acetate, thereby resulting in good adhesion on both surfaces. In contrast, a lacquer type adhesive would adhere well to the acetate sheeting only, whereas an aqueous base adhesive would adhere only to the paper and not to the acetate sheeting.

Emulsion adhesives are used for carton sealing, tube winding, and for the combining of special papers. High-solids (55%) resin-emulsion adhesives have been suggested for the combining of corrugated board.[35] The chief disadvantage of emulsion type adhesives lies in their high cost, but on a dry solids basis, they are less expensive than the lacquer types. Very thin films should be used, since their use promotes fast setting. Emulsion type adhesives are sometimes used in combination with starch, dextrins, animal glue, casein, soybean protein, and other aqueous adhesives.

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[34] S. F. Thune, *Fibre Containers* 86–92 (June, 1944)

[35] W. F. Gillespie, *Fibre Containers* 59–62 (Sept., 1947)

Rubber Latex

Rubber latex is an emulsion type adhesive which is widely used for laminating metal foils to paper. Wrappers for gum and candy are frequently made by laminating a thin sheet of aluminum foil to a paper base with rubber latex. The advantages of rubber latex lie in its strong adhesion for metal and its highly flexible film. Rubber latex tends to form a skin on the surface which cannot be readily dispersed again.

A small amount of casein, glue, or technical gelatin is sometimes added to rubber latex to act as a stabilizer and prevent coagulation of the latex by the action of the applicator rolls. Clays are frequently added to rubber latex adhesives and, in special cases, vulcanizing agents, such as sulfur and zinc oxide may be added in emulsified form. Materials added to rubber latex should have the same surface charge (negative) as the latex particles to prevent coagulation.

When used by itself, rubber latex forms a water-resistant film. If mixed with starch adhesive, the final bond has only slight water resistance. If latex is to be mixed with a starch adhesive, the starch should contain added alkali in order to prevent coagulation of the rubber particles.

Synthetic rubber latices (butadiene-styrene copolymers, polychloroprene, and butadiene-acrylonitrile copolymers) have been introduced in recent years, and promise to be more useful adhesives than natural latex. These materials are often of complex character and frequently contain curing agents which are added to increase the water resistance or strength of the final bond.

Asphalt Emulsions

Bituminous emulsions are sometimes used for laminating. These emulsions are similar to the usual asphalt emulsions, except that the bitumen is plasticized so that it is of a tacky nature. The dispersed particles of asphalt are about 1 to 4 microns in diameter.

Asphalt emulsions are usually mixed with starch or other adhesives; the emulsion acts principally as an inexpensive extender. Borated starch adhesives do not work well with asphalt emulsions, but plain oxidized starches produce good results. Some asphalt emulsions do not add much to the water resistance of the starch film or even produce a very water-resistant film by themselves. Recently, however, new asphalt emulsions have been produced for which increased water resistance is claimed.

Resin Emulsion Adhesives

Resin emulsion adhesives consist of a resinous material dissolved in an organic solvent and emulsified in an aqueous medium. Emulsions can be produced in this way which are stable against aging, dilution with water, and agitation. The large number of resinous materials which are available makes it possible to produce resin emulsion glues having widely different properties, i.e., emulsions can be selected for particular properties such as water resistance, grease resistance, and solids content. Plasticizers can be added to control the hardness and flexibility of the film. Special solvents may be added to aid in the penetration of lacquer coatings, cellophane, cellulose acetate, or similar surfaces.

Polyvinyl acetate emulsion without solvent phase is used as an adhesive, often in combination with starch. For best results, the laminated sheets should be heated at 100 to 125° C. to bond the resin. Acrylic acid esters in emulsion form are also used as adhesives, often in pressure-sensitive or heat-sensitive self-sealing tapes. These resins have better aging characteristics than natural rubber latex and retain their tack better. They are compatible with synthetic rubber latices and other synthetic resins and often act as plasticizers and modifiers for the dry film.

Certain of the rosin derivatives, such as the hydrogenated methyl ester of abietic acid (Hercolyn) and methyl ester of abietic acid (Abolyn), are used in emulsified form as adhesives. They are recommended for use with starch. Pentaerythritol abietate is sometimes used with rubber latex to improve the stability. The rosin-derived alkyd resins (Neolyn resins) can be emulsified and blended into latex type adhesives to improve the strength, flexibility, and adhesion. These resins can be emulsified by dissolving in xylene and then emulsifying with the aid of potassium hydroxide and oleic acid and stabilizing with ammonium caseinate. There are many other materials which can be used as emulsion type adhesives, but the above serve as typical examples.

Lacquer Type Adhesives

Lacquer type adhesives are useful for bonding materials which are impervious to water and cannot be laminated with the aqueous or emulsion type adhesives. Moistureproof cellophane and varnished or lacquered papers are examples of materials which cannot be bonded with aqueous adhesives, because the adhesive will not wet the surface, and there is no way for the glue line to dry out. Lacquers work satisfactorily on these surfaces, because the solvent in the lacquer will penetrate these surfaces. Lacquer adhesives are also useful for the bonding of porous to non-porous surfaces, such as the pasting of paper labels on glass or metal containers.

Lacquer type adhesives are useful for laminating two paper surfaces where a minimum of distortion or curling is desired. The solvents used in lacquer adhesives do not swell the fibers, and consequently, there is no distortion of the paper and no problem of swelling, curling, or warping. This feature is particularly useful where the paper must be pasted under close tolerance (such as the pasting of map papers on a globe), or when no curling can be tolerated (such as in photographic mounting). The high cost of lacquer adhesives limits their use to specialty uses. Bleeding of the ink on the surface of the paper sometimes results from the solvent in the adhesive.

The same general considerations apply in the formulation of lacquer type adhesives as prevail in the use of these materials for protective coatings. Most of these factors will be discussed later and the reader is referred to the chapter on coating with resinous materials. As a rule, solvents with high evaporating and diffusing rates are desired for adhesive purposes in order to increase the rate of setting. This is in contrast to the delicate balance of solvent mixtures required in lacquers for surface coating, where the film characteristics are of primary importance.

Modified vinyl acetates can be used as solvent adhesives. These produce dried films which are tough and flexible and have good adhesion to non-porous surfaces. Polyvinyl acetate dissolved in methyl acetate, acetone, hydrocarbons, or similar solvents is particularly effective on cellulose acetate sheeting. Polyvinyl chloride acetate can also be used, and a typical formulation is:[36]

20 parts polyvinyl chloride acetate
32 parts methyl ethyl ketone
32 parts cyclohexanone
16 parts propylene oxide

These adhesives are used for sealing cups for hot drinks.

An example of a nitrocellulose lacquer adhesive is:[37]

4-5 parts nitrocellulose
1 part plasticizer
100 parts of mixture containing 40% solvent and 60% non-solvent

Either synthetic or natural resins can be added. In some cases, a much higher percentage of plasticizer may be required. Nitrocellulose adhesives are suitable for joining moistureproof regenerated cellulose sheeting.

A very tacky, high-viscosity cement can be made by dissolving rubber in gasoline, naphtha, benzene, carbon tetrachloride, trichloromethylene, or similar solvents. The viscosity depends upon the degree to which the rubber is masticated and the amount of added filler. Dammar, manila, ester gum, coumarone-indene are examples of resins which are sometimes added to rubber cements.

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[36] J. Del Monte, *The Technology of Adhesives*, p. 124, Reinhold Publishing Corporation, New York, N. Y. (1947)

[37] A. C. Ritman, U. S. 1,969,477 (1935)

An example of a lacquer made from rosin is:[38]

Rosin	29–70%
Venetian turpentine	70–29%
Diethylene glycol ether	1–20%

A suitable adhesive for many papers can be made by dissolving manila resin in alcohol and an aromatic thinner. Shellac dissolved in alcohol has been used for pasting labels. Hydrogenated methyl esters of rosin (Hercolyn resins) can be used in solution form in combination with a film-forming resin and non-film-forming resin to produce adhesives which vary from non-tacky adhesives to pressure-sensitive adhesives. Glycol esters of hydrogenated rosin (Staybelite resins) can be dissolved in suitable solvents to produce a very tacky adhesive. These resins can be mixed with rubber, ethylcellulose, chlorinated rubber, polybutene, and nitrocellulose lacquer adhesives. The coumarone-indene resins can be used in solvent type adhesives of the rubber cement type or the pyroxylin cement type. The phenol-modified grades are recommended.

Hot-Melt Adhesives

Hot melts are discussed in the chapter on coating with resinous materials (see p. 1307). Laminating with hot melts is similar in many ways. The materials used in hot-melt adhesives are waxes or wax-like solids. A typical mixture is composed of a wax, a synthetic resin, and a plasticizer, but more complex mixtures are often used. Hot-melt adhesives are very fast-setting.

Hot-melt adhesives are particularly useful for laminating materials which are impervious to water or organic solvents. They can be used for combining glassine, chipboard, kraft, cellophane, cellulose acetate sheeting, metallic foils, etc. The most important use for hot-melt adhesives is in the manufacture of water-vaporproof laminants, where the hot melts not only function as the adhesive, but also serve as a continuous moisture-resisting film. Products laminated with hot melts combine the advantages of an impregnated and a surface-coated paper. A continuous wax barrier is present, as in the case of a coated paper, yet the film is protected from scratching and marring because it is sandwiched between two protective layers of laminant. The film of adhesive must be unbroken to be effective as a water-vapor-resistant barrier, and no fibers may extend through the film to act as a wick for transferring moisture across the barrier. The wax which penetrates the paper is ineffective so far as moisture vapor-resistance is concerned, since only the wax which exists as a continuous film is effective in holding back water vapor. Products laminated with hot-melt adhesives are resistant to oil, grease, water, dilute acids and alkalies, as well as to water vapor. Some of the products commonly packed in hot-melt laminated products of the heat-sealing type are coffee, potato chips, tea, and dehydrated sops. Hot-melt coatings for subsequent heat sealing are also used for making papers labels.

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[38] J. E. Glegg, U. S. 1,948,334 (Feb. 20, 1934)

Most hot melts are supercooled liquids, which means that they exhibit after-flow if the laminated product is stored under warm conditions. This causes the film to migrate into the paper, leading to a loss in water-vapor resistance. At very low temperatures, products laminated with hot melts tend to become brittle. The strength of hot-melt bonds is dependent upon the rate at which the disrupting force is applied. For example, if subjected to a continuous tension, sheets laminated with hot melts rupture at lower tensions than if the force is applied quickly.

Applying Hot Melts

Most hot-melt laminating is carried out at a temperature below 350° F., and usually in the range of 150 to 250° F. The melt is applied in a molten state to one of the sheets, and then is combined with a second sheet by the application of pressure in a set of squeeze rolls. The laminating operation is continuous and requires careful control of the temperature and speed of the machine in order to obtain a continuous film of melt between the two plies. For best results, the temperature of the melt in the pan should be about 15 to 20° F. above the melting point of the melt, depending upon the speed of the machine and the distance between the waxing and combining rolls. The temperature of the glue line should be slightly above the setting point of the melt by the time the combined sheet reaches the squeeze rolls. If the glue film is hotter than this, it will be too fluid and will tend to soak into the board to an excessive degree. If the glue film is much colder, it will not be liquid enough to produce a good bond with the second ply. The film of adhesive tends to solidify when it comes into contact with the second ply, due to the cooling effect, and this prevents further penetration of melt into the paper. In some cases, the press rolls may be cooled to speed up solidification.

Papers Used for Hot-Melt Laminating

The type of paper used in hot-melt laminating is an important factor. High-density papers are desirable because they absorb less melt and tend to keep the melt on the surface of the paper. However, high-density papers are more difficult to laminate than porous papers. For very hard, non-porous surfaces, melts are required which have a high degree of adhesion for the surface to be laminated. Tensile strength of the melt may have to be sacrificed to adhesive quality, but even so, the rupture of the laminated product usually occurs at the interface between the wax film and the laminant. Melts of lower adhesive strength may be used on porous papers, because the laminated products usually rupture within the paper anyway. When a hard surface is to be laminated to a porous surface, the hot melt must be sufficiently tacky to adhere to the hard sheet. The rupture of such a laminated sheet usually occurs at the interface between the wax and the hard-surfaced sheet. When combining two dissimilar sheets, best results are obtained by applying the hot melt to the denser and harder-surfaced sheet, and then allowing a short time interval before combining with the porous paper. This prevents absorption of the melt into the porous paper and insures the formation of an unbroken film. It also aids the melt in adhering to the dense sheet.

Wax Adhesives

Paraffin is sometimes used for laminating, but tends to produce brittle films and relatively weak bonds. Blends of paraffin with polyisobutylene resins may be used when improved bonding and flexibility are desired.

Microcrystalline waxes are better suited as adhesives than paraffin because of their greater tackiness, greater film flexibility, greater grease resistance, greater water and water-vapor resistance, and greater adhesiveness. The adhesion of microcrystalline wax (as measured between two strips of cellophane) varies from 45 to 320 g. per square inch, whereas paraffin wax has zero adhesion under the same conditions.[39] The plastic types of microcrystalline waxes are preferred, particularly when non-porous materials, such as cellulose acetate foil, are to be laminated. In general, the adhesive strength of microcrystalline waxes increases with the tensile strength of the wax,[40] but is not affected by the melting point and hardness of the wax.[41] Oil in the wax tends to lower the strength.

The consumption of wax in laminating depends upon the type of paper used. It varies from about 2½ lb. per 1,000 sq.ft. for glassine papers to 4 to 10 lb. per 1,000 sq.ft. for porous papers.

Asphalt Adhesives

Asphalt or bitumen products are sometimes used for laminating. Asphalt has a high degree of ductility and tackiness and a high viscosity in the molten state, but has a black color and a bad odor. The bad odor prevents the use of ordinary asphalt on paper for packaging foodstuffs, but there are specially processed asphalts with reduced odor. One method of treating asphalt is to blow steam or air into the molten product to produce blown asphalt. The treated product produces a tougher, more flexible film, and is less susceptible to temperature change than natural asphalt.

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[39] A. Kinsel and H. Schindler, *Paper Trade J. 128*, No. 5: 45–47 (Feb. 3, 1949)

[40] F. W. Padgett and R. B. Killingsworth, *Paper Trade J. 122*, No. 19: 201–207 (May 9, 1946)

[41] A. Kinsel and H. Schindler, *Paper Trade J. 128*, No. 5: 45–47 (Feb. 3, 1949)

Asphalt is used for combining solid fiber and corrugated paperboard, and for the laminating of mutli-ply wrapping and packaging papers. A layer of asphalt between two of the plies in laminated board serves to increase the water-vapor resistance of the board. An asphalt duplexed sheet was used during World War II for making highly water-resistant overseas shipping cases. The asphalt layer was put close to the surface of the board where it functioned as a barrier to the penetration of water. Asphalt-laminated paperboard is widely used for cookie boxes.

Asphalt is applied at a temperature around 275° F., or about 100° F. above its softening point. The equipment most generally used consists of a heated pick-up, a set of rubber-covered press rolls, and a number of cooling rolls. The pick-up roll revolves in the molten asphalt and picks up the asphalt and applies it to the paper. The asphalt is usually applied to the liner stock, and then the filler stock brought into contact a few seconds later. If the filler is warm when brought into contact with the asphalt film, a stronger bond is produced. The high temperature of application (made necessary by the high viscosity of asphalt) results in excessive absorption of asphalt by the paper. The high temperature also tends to dehydrate the paper.

One disadvantage of asphalt is that it tends to bleed from the glue line of the combined board on standing. This is particularly bad when thin sheets are used, as in the case of asphalted crepe papers. The bleeding resistance of asphalt-laminated papers is measured by sandwiching the test sheet between two pieces of smooth white paper and holding at 150° F. at a pressure of 0.5 p.s.i. for five hours.[42] The white paper is then examined for staining.

Asphalt is sometimes used in combination with other hot-melt materials, such as petroleum waxes, pentaerythritol resins, rosin esters, hydrocarbon terpene resins, and coumarone-indene resins. These materials add toughness and tack to the asphalt and, in some cases, improve the flexibility and water-vapor resistance. Reinforcements, e.g., jute, sisal, cotton, or burlap, in the form of cord or fabric may be incorporated in the asphalt layer when making laminated papers. Many grades of asphalt-laminated papers are creped.

Resin Adhesives

The natural and synthetic resins are frequently used in blends with waxes, asphalt, and other hot-melt adhesives. These resins are added to increase the toughness of the adhesive and, in some cases, to increase the water-vapor resistance. Certain hot-melt adhesives are entirely composed of resins. These are used for pasting paper labels on metal cans and for the laminating of metal foils. A wide variety of different formulas are used, and a few typical examples are given below.

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[42] See TAPPI Standards

Ethylcellulose is sometimes used in hot-melt adhesives. When properly compounded with other ingredients, ethylcellulose produces a fast-setting adhesive which has good heat-seal properties. Ethylcellulose hot melts are suitable for bonding paper, cellophane, metal foil, glassine, or other similar materials. A formula for a hot-melt adhesive containing ethylcellulose is:[43]

Ethylcellulose (10–20 cps.)	5–20 parts
Wax (carnauba, spermaceti, montan, beeswax, etc.)	0–20 parts
Mineral wax	15–30 parts
Plasticizer	0–10 parts
Resin	40–65 parts

Low-viscosity polyvinyl acetate makes an effective hot-melt adhesive. Plasticizers are generally added to increase the flexibility, to lower the heat-sealing temperature, and to reduce the melting point. Natural resins such as dammar, may be added to lower the melting point. A suitable formula is:

80 parts vinyl chloride acetate resin
20 parts modified alkyd resin
Plasticizer such as dibutyl phthalate

The coumarone-indene resins are well suited for hot-melt adhesives because of their low melting point (110–130° C.), thermal stability, and good tack. The hydrogenated and phenol-modified grades are useful because of their high degree of compatibility with synthetic resins. Coumarone-indene resins can be mixed with rubber derivatives, ester gum, shellac, waxes, paraffin, oils, and most organic solvents except the alcohols. The unmodified grades can be used in combination with nitrocellulose. The phenol-modified grades can be used in combination with polystyrene and cellulose acetate. The chlorinated diphenyls make good plasticizers. A suitable formula combining coumarone-indene resin with ethylcellulose is:[44]

Ethylcellulose (20 viscosity)	15
Coumarone-indene resin (Nevilla R-7)	50
Rosin derivative (Staybelite)	15
Dibutyl phthalate	20

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[43] Tech. Bulletin, "Ethocel Hot Melts for Paper Coatings," Plastics Division, The Dow Chemical Company, Midland, Michigan

[44] "Neville Resins and Plasticizers," The Neville Co., Neville Island, Pittsburgh, Pennsylvania

Rosin is not well suited for hot-melt laminating because of its bad odor and poor stability. However, certain of the rosin derivatives, such as hydrogenated methyl ester of abietic acid (Hercolyn), the ethylene glycol esters of hydrogenated rosin (Staybelite), and the ethylene (or diethylene) glycol esters of rosin (Flexalyn), make effective adjuncts to hot-melt adhesives. These can be used with nitrocellulose, ethylcellulose, polyvinyl compounds, and rubber to increase the tack and improve the flexibility of the film. Biddle[45] suggests the following formula:

8 parts ethylcellulose
42 parts hydrogenated methyl ester of rosin
50 parts hydrogenated rosin

Another formula is:[46]

10 parts ethylcellulose
63 parts ethylene glycol esters of hydrogenated rosin (Staybelite)
27 parts paraffin

The rosin-derived alkyd resins (Neolyn resins) are also suitable for hot-melt adhesives. Some of these resins have enough flexibility and sufficient strength to be used by themselves, but they are generally used in combination with other film-forming resins, such as vinyl chloride-acetate copolymers. A suitable formula requiring an application temperature of about 200 to 250° F. is as follows:[47]

80% rosin-derived alkyd (Neolyn)
10% vinyl chloride-acetate (Vinylite VYHH)
10% di-2-ethyl hexyl phthalate

Products with higher melting points can be made by eliminating the phthalate and using a Santicizer resin.

The rubber derivatives, cyclized rubber and chlorinated rubber, and some of the synthetic rubbers, can be used in hot-melt adhesives. The rubber adds water–vapor resistance, flexibility, and adhesiveness to the film, but increases the viscosity of the melt. The butyl rubbers are effective in increasing the bonding strength of wax melts.

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[45] A. Biddle, *Paper Trade J. 122,* No. 23: 252–258 (June 6, 1946)

[46] Tech. Bulletin, "Ethocel Hot Melts for Paper Coatings," Plastics Division, The Dow Chemical Company, Midland, Michigan

[47] "The Neolyns, A New Series of Resins," Synthetics Department, Hercules Powder Co., Wilmington, Delaware

CHAPTER XXI

INTERNAL TREATMENT OF PAPER WITH RESINOUS MATERIALS

The following material is concerned with the internal treatment of paper with plastics and resinous materials. It has been subdivided into sections, treatment of paper with latices and emulsions, saturation of paper (with asphalt, oils and waxes), and paper plastics.

Treatment of Paper with Latices and Emulsions

Latices and emulsions can be applied to paper by internal application (beater addition) or by surface treatment (tub sizing or saturation). Natural rubber latex, reclaimed rubber dispersions, synthetic rubber latices, synthetic resin emulsions (e.g., acrylic, polystyrene, vinyl, and alkyd), and oil emulsions are some of the emulsion type materials used.

The results of beater addition depend upon the type of resin used, method of application, and the amount of resin absorbed by the paper. If a high percentage of resin is added, the paper takes on the properties of the resin, resulting in a product of high toughness, wearing, and tearing resistance. Some of the common products made by internal treatment of paper with resins are artificial leathers, shoe parts, wrapping papers, gasket papers, and paper base tapes. Artificial leathers are usually coated after treatment. Internal treatment of paper with resins is used when a finished product is desired having such properties as toughness, softness, flexibility, stretch, initial or edge tear, and strength at sewn seams. The tensile strength and stiffness of the paper may be reduced by treatment.

Properties of Beater-Treated Papers

Beater addition is the simplest method of incorporating resinous materials in paper, inasmuch as no special equipment is required. However, there are several serious disadvantages to beater application, particularly when large amounts of resinous materials are added. Among the most serious disadvantages are excessive white water losses, foaming, fouling of equipment, slow drainage on the machine, and two-sidedness of the paper. Some of these difficulties have been overcome by the introduction of new types of resin latices, but there are still many cases where beater addition is not satisfactory.

Beater-treated papers have radically different physical properties from papers saturated in the dry condition. In general, beater-treated papers are tougher, stronger, and better able to retain their strength after creasing than dry-saturated papers. These advantages are derived from the fact that a greater number of fiber-to-resin bonds are produced by beater addition, compared with the number produced by the saturation of dry paper. While saturation of dry paper results in a coating of resin on the fibers which tends to flow away from the fibers during molding, beater addition produces resin bonds which remain in place and are further strengthened during molding.[1] In the case of beater-treated papers, the fibers are free to slide past one another during molding, thus re-forming the sheet into a more homogeneous material.

Types of Resins Used in Beater Treatment

Both elastomer (rubber) latices and resin emulsions are used for beater addition. The principal use for elastomer latices in beater treatment has been for the manufacture of tough, leather-like products in which relatively large amounts of elastomer are used. A typical grade is fiberboard, a very tough and pliable board which is used in shoes as stiffeners, counters, innersoles and heels. About 20% rubber latex is generally incorporated in the board to impart the necessary pliability, wet strength, and resistance to wear. The board is made on a wet machine where the sheet is formed continuously on a cylinder mold until a layer of the desired thickness is obtained. This layer is then cut loose and laid out in sheet form, after which it is pressed, kiln-dried, and finally calendered. Pressing is necessary to cause the rubber particles to adhere to one another, and thereby bring out the rubber-like characteristics in the paper. Pulp treated with small amounts of elastomer latices has improved strength properties and increased wet strength.[2]

Among the resin emulsions used for beater addition are the polystyrenes, alkyd, polyalkylacrylate, and phenolic resins. The use of resins for beater addition is discussed in a later section on paper plastics.

Methods of Applying Latices in Beater Treatment

Best results in beater treatment are obtained by using unbeaten or lightly beaten pulps, because this gives the maximum number of resin-to-fiber bonds. The retention of resin in the paper increases with increased beating up to a certain point, after which it levels off. The type of pulp is important, rag stock being preferred over sulfite or sulfate for the development of maximum physical properties. However, a considerable amount of chemical wood pulp is used because of the lower cost, and it is also quite common to use a mixture of rag with either sulfite or sulfate. Yost and Aiken[2a] found in the case of rubber (nitrile) latex that bleached pulp (sulfate) had a greater tolerance for the latex than unbleached pulp when the pulp was unbeaten, but that beating increased the tolerance with the unbleached pulp but not with the bleached pulp.

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[1] F. H. Snyder, L. Spiwak and A. E. Moyer, *Tappi 33,* No. 4: 87A–90A (Apr., 1950)

[2] R. H. Walsh, H. H. Abernathy, W. W. Pockman, J. R. Galloway and E. P. Hartsfield, paper presented at the 35th Annual Meeting of TAPPI, New York City (Feb., 1950)

One of the principal objections to beater addition has been the high percentage of material lost in the white water, a serious problem when ordinary anionic latices are used in an open system. Three principal methods are used to improve the retention of latex in the paper. These are: (*1*) alum precipitation of the latex, (*2*) pretreatment of the fibers to impart a positive charge which attracts the negatively charged latex particles, and (*3*) the use of positively charged latices.

Originally, alum precipitation of the latex was the only means of increasing the retention of latex. This method consists of mixing an anionic latex with the stock in the beater, followed by the addition of sufficient alum to lower the *p*H to the isoelectric point of the latex. One disadvantage of this method is severe fouling of the beater, because of the deposition of latex particles. The retention is fairly good with rag and sulfate stock, but is generally poor with sulfite stock. The poor retention with the latter is due to premature coagulation of the latex resulting from the acid character of sulfite fibers. This leads to the formation of relatively large coagulated particles which are not retained well in the stock. Buffering the stock to a *p*H of 8.0 to 8.5 with alkaline salts aids in retention.

An important advance in beater treatment with elastomer latices was the development of a method for the pretreatment of the fiber to change its electrostatic charge from negative to positive. The best-known process of this type is the Bardac process, developed by the American Cyanamid Company, in which a melamine-formaldehyde acid colloid is used to impart a positive charge to the fibers before the latex is added.[2b] By using this process, relatively large amounts of latex can be retained in the stock without serious white water losses or fouling difficulties. Between 1 to 5% of melamine resin is used to impart the desired charge to the fibers, and this is followed by 10 to 50% of resin latex, such as polystyrene, polyethyl acrylate, vinyl, etc., to obtain the desired properties in the finished paper.

It was first thought that the melamine-treated pulp in its positively charged condition attracts and adsorbs negatively charged anionic latices (e.g., GR-S and Hycar). Subsequent theory, however, seems to indicate that the positive fiber does not directly adsorb the emulsion particles, but instead inactivates a small amount of the negatively charged emulsifying agent acting as the latex stabilizer. This reduces the stability of the latex emulsion particles, causing them to be deposited on the fiber surface. Emulsions containing an excess of emulsifier are not deposited, even though part of the emulsifier is adsorbed or neutralized by the fiber. Only that part of the melamine resin acid colloid adsorbed on the fiber is effective in fixing the emulsion particles at the fiber interface; any unadsorbed resin colloid merely coagulates the emulsion in the aqueous phase. A general procedure for incorporating rubber latex in kraft paper using the Bardac process is given below. All data are expressed on a dry basis.

[2a] D. M. Yost and W. H. Aiken, "Effect of Certain Papermaking Variables upon Beater Addition of Nitrile Rubber Latices," Tappi Paper-Plastics Conference, Syracuse, N. Y. (Oct. 19–20, 1950)

[2b] L. H. Wilson, C. S. Maxwell and C. G. Landes, Can. Pat. 450,523 (Aug. 17, 1948)

(*1*) Of prime importance in the Bardac process is the hydrogen-ion concentration, since slight alterations affect the adsorption of the acid resin colloid which, in turn, affect the retention and loss of the latex or resin dispersion. The *p*H of the pulp system should be adjusted between 5.0 to 5.5 with 5% acetic acid before beating (assuming the pulp to have an initial *p*H of 8.0, it will take approximately 1% of acid on the pulp) after which the pulp should be beaten to a Canadian freeness of about 600 to 650.

(*2*) 2% of melamine resin (Parez Resin 607) should be added to the pulp from a 6% solution previously prepared and stored for at least twenty-four hours. In order to obtain the best possible adsorption of the resin colloid, it is important to provide adequate contact time between the resin colloid and the pulp. Although most of the adsorption takes place within the first few minutes, thirty minutes to one hour contact has been found to give best results. The *p*H should be between 4.5 to 5.0 during the contact period. No further additions of acetic acid are required to adjust to this *p*H, since the addition of the acid resin colloid will generally suffice to lower the *p*H to the desired value.

(*3*) After the prescribed contact time, the *p*H of the system should be raised to between 6.5 to 7.0. It is preferable to use sodium aluminate (about 1% on the fiber), but sodium bicarbonate can be used (approximately 2% on the fiber). The alkali should be added in the form of a 10% solution. (Coagulation of the disperse phase of the latex is accelerated by low *p*H values and adsorption is retarded by high *p*H values.)

(*4*) About 20% latex (dry solids to dry fiber) is next added to the stock, after the latex has first been compounded with stabilizer and anti-oxidant and the total solids reduced to 10% by weight with tap water. The pulp plus acid colloid plus compounded latex appears as a milky slurry, but upon circulation, the system should clarify completely to a water-white appearance. The circulation time may be as short as thirty minutes and as long as two hours, depending upon the concentration of the melamine resin adsorbed, the *p*H, the nature of the stabilizers and emulsifiers in the latex, and the concentration of disperse resin or rubber phase on the fiber. Jordaning or any violent agitation should be avoided in order to prevent a disturbance to the fiber-resin bond.

(*5*) The pH should finally be adjusted between 5.5 to 6.0 with a 5% alum solution in order to coagulate any small amount of residual latex which has not been adsorbed after a reasonable contact time.

In addition to the Bardac process, there are two other somewhat similar processes—the neoprene latex (du Pont Process) and the phenolic resin (Snyder Process). In the first of these, latex particles (up to 50% of the fiber weight) are deposited on the fibers by a controlled flocculation procedure using alum or other polyvalent salt as the precipitant. The latex is stabilized (with naphthalenesulfonic acid-formaldehyde condensation product) and sensitized with alum before addition to the beater, but the *p*H is maintained on the alkaline side. Coagulation in the beater is obtained by lowering the *p*H of the stock to about 4.5 with alum. Vulcanizing agents and antioxidants can be mixed with the stock prior to the addition of the latex. In the other (Snyder) process, a special phenolic resin is used to precipitate fairly high percentages of latex on the fiber. The latex is added first to the beater, followed by the phenolic resin and then by a precipitant consisting of an acidified alum solution.

Another more recent method of obtaining a high retention of elastomer latices in beater addition is by the use of positively charged (cationic) latices. These latices have a natural affinity for the fiber and are added to the pulp by an exhaustion procedure. The original work on cationic latices was done in England in the production of a positively charged natural rubber latex called Positex.[3] Some of the other elastomers now available in positively charged latex form are Neoprene,[4,5] nitrile rubbers, and GR-S.

Protective colloids, anti-oxidants, vulcanizing agents, and plasticizers are generally emulsified with the latex prior to addition to the beater. The natural anti-oxidants in natural rubber latex are mostly lost in the white water, but these are compensated for by the addition of more effective synthetic anti-oxidants emulsified with the rubber.

External Application of Resins to Paper

The two principal methods of external application of resins to paper are the tub-sizing method and the off-machine saturation method. In the first method, the tub-sizing method, the paper is treated on the paper machine in a partially dried condition. A relatively small percentage of resin is added to the paper by this method, and while the physical and chemical properties of the paper are greatly improved, the final product must still be regarded as paper. In the second method, the off-machine saturation method, the treatment is carried out in a separate operation and the paper is dry at the time of saturation. Ordinarily, a high percentage of resin is added by this method so that the final product takes on the properties of the resin.

[3] C. M. Blow, Positex Pamphlet No. 1, "Positex in the Paper Industry," The British Rubber Dev. Bd., Market Building, Mark Lane, London, E. C. 3

[4] R. H. Walsh, H. H. Abernathy, W. W. Pockman, J. R. Galloway and E. P. Hartsfield, paper presented at the 35th Annual Meeting of TAPPI, New York City (Feb., 1950)

[5] E. G. Partridge, *Paper Trade J. 127*, No. 6: 45–48 (Aug. 5, 1948)

After saturation, the paper is passed between squeeze rolls to remove excess saturant, after which heat is applied to drive off the water and set the resin. Heat increases the adhesion between the resin and the fibers and increases the strength. The maximum increase in burst, tensile, and elongation is obtained by heating to the softening point of the resin.[6] However, too high a temperature for prolonged periods results in thermal degradation of the paper and oxidation and degradation of the resin. Stepwise drying is desirable successively to eliminate the water, set the resin, and finally sinter the resin. The temperature should be slightly lower than the melting point of the resin at the first few driers and then should be increased to about 20 to 30° higher than the melting point at the last few driers. In general, saturation produces a softer, more flexible sheet than beater addition[7] because of the greater continuity of resin.

Types of Paper Used for Saturation

The paper used for saturating with latices or emulsions is generally a kraft, sulfite, or a rag paper of high alpha cellulose content, although papers made from soda pulp have been used. In some cases, the paper may contain an inert filling material, e.g., ground leather. The paper should be very loosely felted and should have an apparent density varying from 4.0 to 7.5.[8] It must be made with very little beating, pressing or calendering, and must be unsized.

The moisture content of the paper at the time of saturation is one of the most important variables. Papers with a normal or higher-than-normal moisture content are required, since it is almost impossible to saturate dry, non-porous papers such as well-beaten kraft.[9] On the other hand, almost any type of paper can be saturated in the wet state, inasmuch as latex particles will penetrate along the water-filled pores, because of Brownian movement. The presence of water in the pores permits uniform infiltration of latex particles, and hence saturation of a wet sheet tends to be more uniform than saturation of a dry sheet.

Types of Resins Used for Saturation

Elastomer latices, including both natural and synthetic rubbers, are used extensively for the saturation of paper for making artificial leathers. The latex is generally applied at a solids content of 5 to 35%, and the paper is immersed for a period of seven to ten seconds. The pick-up is about 20 to 100% of dry solids on the weight of the paper, 30% being an average

[6] A. W. Oliner and F. W. O'Neil, *Paper Trade J. 125,* No. 7: 73–80 (Aug. 14, 1947)

[7] A. F. Owen, *Tech. Assoc. Special Report 359,* Minutes of the Plastic Committee, p. 49 (July 31, 1945)

[8] R. T. Nazzaro, *Tappi 33,* No. 1: 23–25 (Jan., 1950)

[9] M. J. Vittengl, *Paper Mill 61,* No. 1: 15–18, 20 (Jan. 1, 1938)

figure. This amount of saturant greatly increases the tear and wearing resistance of the paper and greatly increases the stretch.

Natural rubber latex imparts an unusual combination of physical and chemical properties to the paper, but it presents problems in stability, aging, non-uniformity, and odor. In many respects, synthetic rubber latices are superior to natural rubber latex, particularly when oil resistance and resistance to aging are important. Some of the synthetic rubbers suitable for saturating paper are the chloroprene polymers (neoprene), the butadiene acrylonitrile copolymers (Buna N-GR-A, Hycar OR-25, Hycar OR-15, and Chemigum 200), and the styrene-butadiene copolymers (Buna S-GRS and Dow Latex 512-K, a high styrene type). The copolymers of acrylonitrile and butadiene (Hycar OR-25) are particularly well suited for saturating because of their small particle size.[10] They generally result in an appreciable increase in elongation, flexibility, tensile strength, tear resistance, chemical resistance, and grease resistance. Polychloroprene (neoprene) latex gives high tensile, good tear, and good burst strength, but produces papers somewhat lower in flexibility and elongation than some of the other synthetic rubber latices.[11] Reclaimed rubber dispersions, widely used during World War II, have a larger particle size than the rubber latices and are, in general, typified by inferior physical properties, poor stability, and poor color.

The saturation of paper with synthetic resin emulsions is becoming increasingly important. Resins impart quite different properties to paper than the elastomers or rubber latices. The results depend upon the type of resin, amount added, type and amount of plasticizer and similar factors, but in general, the synthetic resins impart to paper a higher degree of heat, light, and chemical resistance and a lower degree of elasticity than the elastomers.

Among the synthetic resins used for saturation are the alkyds, acrylics, methacrylic esters, polyvinyl acetate, polyvinyl acetate copolymers, vinylidene chloride copolymers, and ethylcellulose (in xylene or aliphatic hydrocarbons). The resin may be applied by dipping, roll coating, or spraying; with squeeze rolls, air knife, or doctor blade being used for removing the excess resin. Properly plasticized vinyl polymers yield products with toughness comparable to that obtained with rubber latex,[12] but vinyl resins and styrene polymers have poorer water resistance than rubber.[13] The acrylates and methacrylates impart a high degree of water resistance, but the tearing strength is lower than that obtained with natural rubber or polyvinyl acetate. Oliner and O'Neil[14] found natural rubber to be most effective, and the vinyl polymers next, followed by the polyvinylidene chloride resins. Alkyd resins have a fast rate of cure, good color, high water resistance, and good electrical properties, but they produce papers of low strength. Resin emulsions are sometimes used in combination with elastomer latices. A comparison of results obtained by saturating paper with several different commercial latices and emulsions is shown in Table I.[15]

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[10] E. G. Partridge, *Paper Trade J. 127,* No. 6: 45–48 (Aug. 5, 1948)

[11] *Idem.*

[12] R. T. Nazzaro, *Paper Trade J. 119,* No. 13: 33–36 (Sept. 28, 1944)

[13] J. Y. Kao, L. Gold, A. Stull, R. Worden and W. Abramowitz, *Paper Trade J. 119,* No. 3: 42–47 (July 20, 1944)

An important factor in saturation is the degree of adhesion which is obtained between the rubber or resin particles and the paper fibers. Adhesion depends upon the structural features of the polymer, the amount and type of modifying agent used, and the degree of pressing and curing of the saturated paper. Among the elastomers, polychloroprene produces papers of very high tensile strength because of its strong intermolecular cohesion, but for the same reason, lateral adhesion to the fibers is poorer than for other elastomers.[16] Commercial styrene-butadiene copolymer (e.g., GR-S) has fair adhesion to paper, but the adhesion decreases as the styrene ratio is increased.[17] Polyvinyl acetate, properly plasticized, exhibits better adhesion to paper fibers than GR-S. Alkyd resins have poor adhesion to the fibers. In general, it may be stated that resins exhibiting high intermolecular forces exhibit poor adhesion to paper fibers unless these forces are weakened by the introduction of plasticizers.

TABLE I

EFFECTS OF RESINS INCORPORATED IN PAPER BY LATEX SATURATION ON PROPERTIES OF PAPER

Type of latex	Sat. bath, total solids	Per cent loading	Tensile lb./in. width	Elongation, %	Burst, p.s.i.	Fold, MIT	Int. tear, g.	Wet tensile, lb./in. width
Copolymers of acrylonitrile and butadiene								
Hycar OR-25	9.9	37.0	15.9	7.7	28.3	112	298	4.6
Hycar OR-15	10.0	40.7	18.6	7.7	(44.8)	434	290	5.6
Acrylic acid ester								
Hycar PA	10.0	38.7	20.6	3.8	29.2	853	281	1.2
Polyvinyl chloride polymer plasticized								
Geon PX-8	12.6	38.1	26.2	3.5	39.2	459	190	8.9

Poor anchorage of the resin to the fibers and migration, which are serious problems with certain resins, can be overcome by special compounding of the latex to render the latex heat sensitive so that the resin is set in place upon drying. There are two principal methods: (*1*) by stabilizing the latex to tolerate normally coagulating salts, e.g., magnesium sulfate, at room temperature, but maintaining sensitivity to the salt at the higher drying temperatures, or (*2*) by adding special complex salts of zinc or other elements with ammonia or amino compounds which are decomposed at the temperatures of drying (Nieley process). With the latter method, the high temperature of drying evaporates the ammonia and liberates the metallic salt which coagulates the resin and prevents migration.

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[14] A. E. Oliner and F. W. O'Neil, *Paper Trade J. 125,* No. 7: 73–80 (Aug. 14, 1947)

[15] Results presented by R. L. Steller of B. F. Goodrich Company at 1948 Plastics Conference, Appleton, Wisconsin (Aug. 16–17, 1948)

[16] R. T. Nazzaro, *Tappi 33,* No. 1: 23–25 (Jan., 1950)

[17] *Idem.*

In addition to the use of plasticizers for improving the adhesion of resin to the fibers, plasticizers are also incorporated in resin emulsions for the purpose of improving the flexibility and aging properties of the resin. The plasticizer should be emulsified with the resin or added later in emulsified form. One difficulty is that plasticizers, particularly the highly polar types, are attracted by the fibers as well as by the resin, thus robbing the resin of its plasticizer and resulting in a loss of flexibility upon aging. Migration and absorption of plasticizer are particularly serious with certain resins (e.g., polyvinyl acetate).

In addition to plasticizers and heat-sensitizing agents, latices for saturation often contain stabilizers, anti-oxidants, and curing agents. These should be compounded with the latex prior to saturation, and unless water soluble, must be added in emulsified form. One of the troubles encountered in saturating with rubber latex is the tendency of the saturated sheet to stick to the squeeze rolls. This can often be overcome by the addition of soap or other surface-active materials. Softening agents for the paper are sometimes added with the latex.

The amount of resin picked up by the paper and the distribution of resin in the paper are determined by the particle size and particle size distribution of the dispersed particles in the latex. The average particle should be around 0.2 to 0.3 micron in diameter, because larger particles tend to block the pores of the sheet and inhibit penetration, a phenomenon referred to as "plating out." The electrostatic charge on the dispersed particles is important because it affects both the stability and the manner in which the latex penetrates the paper. Anionic latices penetrate readily, but tend to migrate during the drying process. Cationic latices tend to exhibit plating out. Non-ionic latices tend to be unstable.

Saturation of Paper with Asphalt, Oils, and Waxes

Certain grades of paper are impregnated with oils, hot asphalt, or molten wax to produce products for special purposes. These materials tend to lower the strength of the paper, but increase the water resistance. Wax-treated papers are discussed in the chapter on coating with resinous materials, but a few of the other grades are discussed below.

Asphalt-Saturated Papers

Asphalt is obtained from the processing of certain petroleum oils, or from naturally occurring asphalt deposits resulting from the partial oxidation of petroleum. Large natural deposits of asphalt occur on the island of Trinidad and in Venezuela. Asphalt is shipped in paper cartons, steel drums, and tank cars.

Asphalt varies from a semi-solid, sticky substance to a hard, brittle material. It consists of a dispersion of solid material in an oily medium. Some asphalts have softening points as high as 300° F., but most grades used in the paper industry have a softening point between 140 to 200° F. Asphalt differs from paraffin in that it has no sharp melting point and has a much higher viscosity. It is very viscous when applied just above its softening point, but becomes quite fluid when heated to about 100° F. above its softening point. Unrefined asphalt is generally used for impregnating and coating roofing papers.

Vegetable pitch (stearine), which is a soft black, tarry substance obtained as the final residue in the manufacture of distilled red oil and stearic acid, is sometimes used in the manufacture of roofing papers by heating and mixing with the other ingredients.

In the saturation of paper with asphalt, paper felt at a moisture content of 3 to 6% is run through a bath containing asphalt at a temperature of about 350 to 400° F. After leaving the bath, the felt is passed over steam-heated rolls to drive the saturant into the sheet and remove any excess from the surface. About 125 to 135% saturant on the weight of the sheet is applied in the case of floor felt, and 140 to 165% in the case of roofing felt.

In the case of roofing felts, a surface coating of asphalt is applied to the saturated sheet and spread evenly by means of steam-heated rolls. Then, while the coating is still hot, the sheet is passed under a hopper where particles of sand, talc, slate flour, shell, or other granular material is sifted on the surface and pressed into the soft asphalt by means of chilled metal rolls.

Paper felts for saturation must have sufficient strength to hold up in the process of saturating. In addition, the paper must have a low moisture content and must be sufficiently porous to absorb a high percentage of asphalt. Waste rags are generally used for making saturating felt and these are cooked under mild conditions and beaten in such a way that the fibers are shortened without too much fibrillation and hydration. The color of the rags is of no importance, inasmuch as they are used predominantly for their strength and not for their appearance.

The saturating properties of roofing felt can be measured by the kerosene test (which measures the total saturating capacity) and the oil penetration or xylene penetration test (which measures the rate of saturation). The kerosene test is reported as the percentage of kerosene which is retained by the paper after displacement of air. In carrying out this test, strips of paper are cut and dried in an oven for one to two hours, after which they are cooled, weighed, and then immersed in kerosene at 25° C. under a vacuum of 28 in. of mercury. After soaking for fifteen minutes, the strips are carefully drained and weighed. Another method is to add kerosene from a burette until the paper is saturated. The kerosene number is then determined as follows:

$$\left(\frac{\text{weight of saturated paper}}{\text{weight of dry paper}}-1\right)\times\frac{1}{\text{specific gravity of kerosene at } 25^\circ \text{ C.}}\times 100$$

The kerosene number varies from about 115 to 235. The saturating capacity of paper for a particular bituminous saturant can be determined by the relationship between the specific gravity of the saturant at 25° C. and the kerosene number.

The saturating rate of the paper is measured by the time required for clear paraffin oil (Saybolt viscosity 253 sec. at 72° F.) to soak through a sample of paper floated on its surface. The rate can also be measured by the time required for xylene to rise by capillarity in a strip of the paper for a distance of 3 cm.

Tracing Papers

The primary requirement of tracing paper is a high degree of transparency so that printed or written matter can be seen through a single thickness of the paper. High-grade tracing paper can be made from highly beaten stock without the addition of added materials. Tracing paper made in this way has good transparency and, in addition, possesses a surface which has excellent writing and erasing qualities.

Other types of tracing paper are made by impregnating paper with a substance having an index of refraction close to that of cellulose so that a transparent sheet results. Vegetable drying oils produce papers with good writing and erasing qualities. On the other hand, mineral oil produces a paper with poor writing properties when sufficient oil is used to give good transparency.[18] Ordinary paraffin is unsatisfactory because of its tendency to crystallize and become brittle. Furthermore, non-polar materials, such as mineral oil or paraffin, tend to wet the graphite in the pencil and bind the particles of graphite to the paper so firmly that erasure is difficult.[19]

Oiled Papers

Fruit wrap, meat wrap, and metal wrapping papers are sometimes treated with paraffin oil to improve the water resistance of the paper and to lubricate the wrapped article. In the case of fruit wrap, oil tends to retard spoiling of the fruit. Oil-treated papers are better than waxed papers for wrapping chilled pork because of the higher gas permeability of oil-treated papers.

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[18] H. L. Vincent, *Paper Trade J.* 95, No. 26: 304–306 (Dec. 29, 1932)

[19] *Idem.*

Paraffin oil is loosely defined, but generally refers to a low-viscosity distillate oil derived from a paraffin type or a mid-continent crude oil. Unlike paraffin wax, it is not a true member of the paraffin family because (even in Pennsylvania oils) there are minor percentages of ring type hydrocarbons, such as the naphthenes. Crude mineral oil is the fraction left after distilling the lighter fractions (i.e., the gasoline, naphtha, and kerosene). To prepare purified white mineral oil, the crude oil is treated with sulfuric acid and washed with alkali to remove the unsaturated and aromatic hydrocarbons. The purified oil is colorless, odorless, and tasteless. Refined oil can be treated for unsaturated hydrocarbons by digesting the oil with an equal amount of 95% sulfuric acid for ten minutes. If the oil turns dark brown or black, it contains a high percentage of unsaturated hydrocarbons.

Low-viscosity mineral oils (about 70 Saybolt at 100° F.) are the grades generally used for the impregnation of fruit wraps. High-viscosity oils (150-300 Saybolt) are used for tracing paper and meat wrap. Oils used for food wrappers should be free of all objectionable odor. Odors frequently occur in oil-impregnated kraft papers, particularly in the bleached grades, where the trouble seems to be caused by bleaching residues left in the paper which have a catalytic effect on oxidation of the oil. One remedy is to add an anti-oxidant to the oil.

Some of the methods used for applying oil to paper are dipping, spraying, and roll coating. Paper will pick up between 16 to 20% of its weight of oil when dipped.[20] Under these conditions, the sheet is definitely oily in feel and appearance. This amount of oil is desirable in wrappers for apples, where one of the main functions of the wrap is to furnish a protective film of oil, but most grades of fruit wrap contain only 5 to 8% oil. In some cases, biphenyl is dissolved in the oil for treating fruit wrap in order to prevent stem rot and blue mold.[21]

Treatment with oil reduces the opacity of the paper. This is caused by the filling in of the pores of the paper with oil and, in the case of low-viscosity oils, by a penetration of oil into the fine pore structure of the fiber. This penetration of oil into the fiber structure further reduces the light scattering and accounts for a slow rise in light transmission as the treated sheet stands.

Stencil Papers

Stencil papers must have high tearing resistance, a high degree of hardness, and high stiffness. The paper must be oil resistant and waterproof. In order to obtain these properties, the paper is impregnated with linseed oil. Certain other grades are made by impregnating with a mixture of gelatin, pigment, and oleic acid.

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[20] J. C. Dean, *Paper Mill News 68*, No. 24: 74-76, 78 (June 16, 1945)
[21] R. G. Mirpley and W. R. Barber, U. S. 2,173,453 (Sept. 19, 1939)

Paper Plastics

Cellulose is the raw material used in the manufacture of plastics such as cellulose acetate, ethylcellulose and cellulose nitrate, which are used for making a wide variety of molded and extruded products. This field is too large to be considered in this book. It is the basis of a large and fast-growing industry, the plastics industry. There are, however, aspects of the plastics industry which are the immediate concern of the pulp and paper chemist. One important field is the manufacture of resin-treated paper laminates, another is pulp molding, and still another is the use of cellulose pulps as fillers in molding compounds. Resin-treated papers are produced in the form of thin sheets and heavy boards, whereas pulp-reinforced plastics are sold in the form of granular molding compounds.

A distinction is made between ordinary resin-treated papers described in the previous sections and resin-treated paper plastics on the basis that resin-treated paper plastics are molded or laminated after impregnation. Ordinary resin-treated papers are sometimes treated by pressing or heating, but they are usually not subjected to the high curing temperatures and pressures which are necessary with paper plastics.

One of the common types of resin-treated paper plastics is a grade known as paper laminates. This product consists of several plies of resin-treated paper which are molded or laminated together to produce a rigid structure in which the paper supplies the mechanical strength and the resin furnishes stiffness, water resistance, and resistance to light and chemicals. Paper-base laminates are widely used in the electrical industry for radio sub-panels, socket bases, transformer covers, and circuit-breaker panels. They are also used as counter and table tops to produce a durable surface resistant to water, oils, greases, alcohol, dilute alkalies, and other reagents. They are used to some extent for structural purposes, but have the disadvantage of low ductility and high brittleness, compared to metals. The specific gravity is about one-half that of aluminum and one-fifth that of stainless steel, but the ratio between tensile strength and specific gravity is lower than that of other common structural materials.[22]

Two types of paper plastics are recognized, resin-filled paper plastics and resin-impregnated paper plastics, depending upon the method by which the resin is incorporated in the paper. Resin-filled papers are made by adding resin to the pulp in the beater, after which a sheet is formed on the machine and dried to a controlled volatile content which can be measured as the loss in weight on heating to 180° C.[23] Resin-

[22] G. K. Dickerman, *Paper Trade J. 118*, No. 26: 239–242 (June 29, 1944)

[23] J. C. Parsell, *Paper Trade J. 126*, No. 16: 199–201 (Apr. 15, 1948)

impregnated papers are made by applying a solution of resin to paper in web form.

Resin-Filled Paper Plastics

Resin-filled paper plastics are referred to as preforms. There are two types of preforms, flat and shaped. Flat preforms are made in the form of flat sheets, whereas shaped preforms are vacuum-fitted to a shape closely conforming to the shape of the final molded product. Shaped preforms are used for deep forms and where high strength contours (e.g., automobile panels) are required. Long-fibered pulps such as rag, which normally do not flow very well, can be used in shaped preforms because of the reduced amount of flow required during molding.

Among the resins used in making resin-filled papers are the phenolics, ureas, melamines, vinyls, polystyrenes, and acrylics. The resin may be added to the pulp as (*1*) a solution or emulsion, which is subsequently precipitated on the fibers, or (*2*) as a finely divided powder.

Phenolic resin emulsions are available which can be added directly to the beater and precipitated by the use of alum and sulfuric or phosphoric acid so that retentions over 90% are obtained.[24] Papers containing 45 to 55% of such a resin are highly plastic in nature and are suitable for low-pressure molding. These resins can be used in combination with synthetic elastomers such as Hycar, GR-S types, neoprene, and vinyl polymers to produce products of very high impact strength and elongation. Their principal use is in the manufacture of hardboard and paper-base laminates.

Polystyrene emulsions for beater addition are available commercially.[25] The emulsion, which has a particle size of about 0.2 micron and a *p*H of 9.5, is added to the stock and precipitated on the fibers with alum at a *p*H of 4.0 to 4.5. The amount of resin solids added varies from 25 to 50% of the weight of the paper, and retention is between 90 to 93%. A hard durable laminate is obtained when the treated paper is molded in a press at 500 p.s.i. and 300° F. for ten minutes.

Finely divided, water-insoluble, pulverized resins generally have a higher molecular weight than the water-soluble and emulsified resins and do not penetrate the fibers excessively during laminating or molding. These resins can be added up to 50% of the fiber weight, but high pressure (2000 p.s.i.) is required for molding. The addition of soybean protein to phenolic resin is said to reduce the tendency of the resin to agglomerate into sticky particles and also to improve the flow during molding.[26,27]

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[24] F. H. Snyder, L. Spiwak and A. E. Moyer, *Tappi 33*, No. 4: 87A–90A (Apr., 1950)

[25] W. B. Morehouse, *Paper Trade J. 129*, No. 21: 465–468 (Nov. 24, 1949)

[26] P. K. Potter, U. S. 2,436,328 (Feb. 17, 1948)

[27] P. K. Potter, U. S. 2,436,329 (Feb. 17, 1948)

Lignin has been tried as a partial or complete replacement for phenolic resins. Lignin produces plastics of lower toughness and considerably higher water absorption than phenolic resins, although plastics with good physical properties can be obtained when up to 75% of the phenolic resin is substituted with soda-process lignin.[28] The lignin can be added as an aqueous solution and precipitated in the stock with sulfuric acid, or lignin which is sold in the form of a powder of about 10 microns in diameter can be added directly to the stock at the beater. In one process,[29] lignin is added to the beater in the proportion of 40% lignin and 60% fiber. The *p*H is adjusted to about 4.5 and glue is added to increase the retention, which can be as high as 95%.[30] Alum lowers the strength of the final product, but increases the water resistance. About 15% of phenolic resin may be added later at the size press to improve the hardness and water resistance of the final molded product. A paper containing 40% lignin added in the above manner and 15% phenolic resin added at the size press can be molded at 750 to 800 lb. pressure at 150 to 155° C.[31]

Some of the problems encountered in beater addition are poor retention of resin, foaming, and reduced speed on the paper machine. In a closed system, resin retention generally runs from 75 to 95%.[32] Long-fibered stocks are preferred from a strength standpoint, but fibers which are too long tend to lower the retention. Retention can be measured by solvent extraction, but this is likely to give low results if the resin has been partially insolubilized by heating.

Resin-Impregnated Paper Laminates

In making resin-impregnated paper laminates, the paper is treated in web form with a solution, emulsion, or suspension of resin. The impregnated paper is then molded or laminated with other plies of impregnated paper.

Methods of Applying Resin. The resin may be applied on off-machine equipment, or it may be applied on the paper machine, either at the wet or dry end. In one process (wet-web process), the wet sheet on the paper machine is carried through a resin bath while the sheet is supported by a wire. The sheet contains up to about 65% water at the time of impregnation. The pick-up of resin depends upon the moisture content of the paper, solids content of the resin solution, viscosity of resin solution, temperature of the bath, speed of the machine, and pressure at the squeeze rolls. Only water-soluble or water-dispersible resins can be used. The fibers are saturated with resin and somewhat embrittled when this method is used.[33]

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[28] S. L. Schwartz, J. C. Pew and H. R. Meyer, *Pulp Paper Mag. Canada 46,* No 10: 771–779 (Sept., 1945)

[29] *Paper Trade J. 125,* No. 14: 157–158 (Oct. 2, 1947)

[30] G. H. Thomlinson, *Tech. Assoc. Papers 31:* 580–582 (June, 1948)

[31] *Idem.*

[32] E. S. Bauer, *Paper Trade J. 125,* No. 3: 28–30 (July 17, 1947)

Another method of adding resin is by a modified surface sizing operation carried out on the paper machine. This method is sometimes used to enrich sheets containing resin added at the beater. It has been suggested that lignin be applied in this way by adding an aqueous suspension of purified lignin (5–10 microns in size) at a concentration of 15 to 20% solids.[34]

Most impregnation is done on off-machine equipment. This consists of treating dry paper with a solution or emulsion of resin. The paper is generally dipped into the resin solution and then is passed under and between two metering rolls, after which the paper is dried to remove solvent and, when thermosetting resins are used, partially to polymerize the resin. The machine may be equipped with sky rolls so that the sheet can be brought out of the resin bath to increase the penetration by releasing air from the paper.[35] Most of the following discussion refers to the treatment of paper with resin solutions on off-machine equipment.

In one process, thin tissue paper is impregnated with an aqueous solution of phenolic resin. The treated paper contains a high percentage of resin and is sold to plywood manufacturers, where it is used alternatingly between layers of plywood to build up an assembly suitable for laminating. When pressure and heat (280–320° F.) are applied to the assembly, the resin in the paper acts essentially as a resin glue line. The paper in this case acts principally as a carrier for the resin. Creped paper is sometimes used when curved shapes are to be laminated.

Resins Used for Paper-Base Laminates. Both thermoplastic and thermosetting resins can be used for paper-base laminates, but thermosetting resins are more widely used because of their lower viscosity in organic solvents, and because they impart the necessary physical properties to the laminate. There are several principal classifications of laminates: mechanical (structural), electrical, punching, and decorative.

Phenolic resins are widely used, particularly in mechanical laminates where water, heat, and electrical resistance are required. For punching grade laminates, phenolic resins specially modified with plasticizers or reacted with drying oils are used to yield laminates having good plasticity and elasticity. The phenolics used in electrical grades are generally catalyzed with ammonia, amines, or other less conductive catalysts in place of the strong alkaline catalysts normally used.[36]

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[33] E. S. Bauer, *Paper Trade J. 125*, No. 3: 28–30 (July 17, 1947)

[34] Cooperative Report of the U. S. Forest Products Laboratory, *Paper Ind. 27*, No. 11: 1683–1689 (Feb., 1946)

[35] F. W. Egan, *Paper Trade J. 121*, No. 14: 137–140 (Oct. 4, 1945)

Urea and melamine resins are used for making decorative laminates. Melamine resins are used where translucent, light-colored products with good heat and water resistance are required. Acrylics, alkyds, polyesters, polystyrenes, and polyvinyl resins are examples of thermoplastic resins sometimes used.

In the thermosetting field, both water-soluble and solvent-soluble resins are used. As a general rule, the phenolic resins are applied from alcohol solution, whereas the urea and melamine resins are applied from water solution. Water-soluble resins are generally used for impregnation on the paper machine, whereas alcohol-soluble resins are most widely used for off-machine treatment. In some cases, no solvent is used, as, for example, with polyester resins, which are used as partially polymerized liquids.

The primary purpose in impregnation is to saturate the sheet with resin so that the final laminated product takes on the characteristics of the resin. If too little resin is present (less than about 30%), the water resistance of the laminate will be low and it will be a poor insulator when wet. On the other hand, the mechanical properties of the laminate are better if small amounts of resin are used. Resin adds compressive strength to the laminate, but maximum all-round strength properties are obtained when the amount of resin is just sufficient to fill all the voids in the paper.

One of the important functions of the resin is to protect the fibers in the laminated product. Low molecular weight (water-soluble) thermosetting resins give the maximum water resistance because they penetrate the fiber where they are subsequently polymerized in the molding operation. Because of their polar nature, these resins result in considerable cross linking with the fibers, which imparts a high degree of dimensional stability and a high degree of water resistance to the laminate, but tends to embrittle the fibers. On the other hand, high molecular weight (solvent-soluble) resins do not produce as water-resistant a laminated product as the water-soluble resins because the resin does not penetrate the fiber as well and there are fewer polar groups to react with the fibers and hence less cross linking. Comparative water absorptions for papers treated with water-soluble and solvent-soluble resins are shown in Figure XXI-1.[37]

For a given varnish, the rate of penetration is directly proportional to the viscosity.[38] Low-viscosity varnishes penetrate better and result in products of better water resistance than high-viscosity varnishes.[39] To obtain a high degree of alkali and water resistance in a laminate to contain 50% varnish, Kline[40] recommends the application of 20% penetrating (low-viscosity) varnish and 30% regular (high-viscosity) varnish. However, if maximum impact strength is desired, the varnish should be of the viscous, non-penetrating type in order to keep the varnish on the surface of the fibers as much as possible.[40] Resins of high degree of polymerization require less polymerization on curing, and consequently shrink less during curing than resins of low D.P.

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[36] C. B. Bennett, paper given at 35th Annual Meeting of TAPPI, New York City (Feb. 20–23, 1950)

[37] C. J. Straka, *Paper Trade J. 126*, No. 14: 184–188 (Apr. 1, 1948)

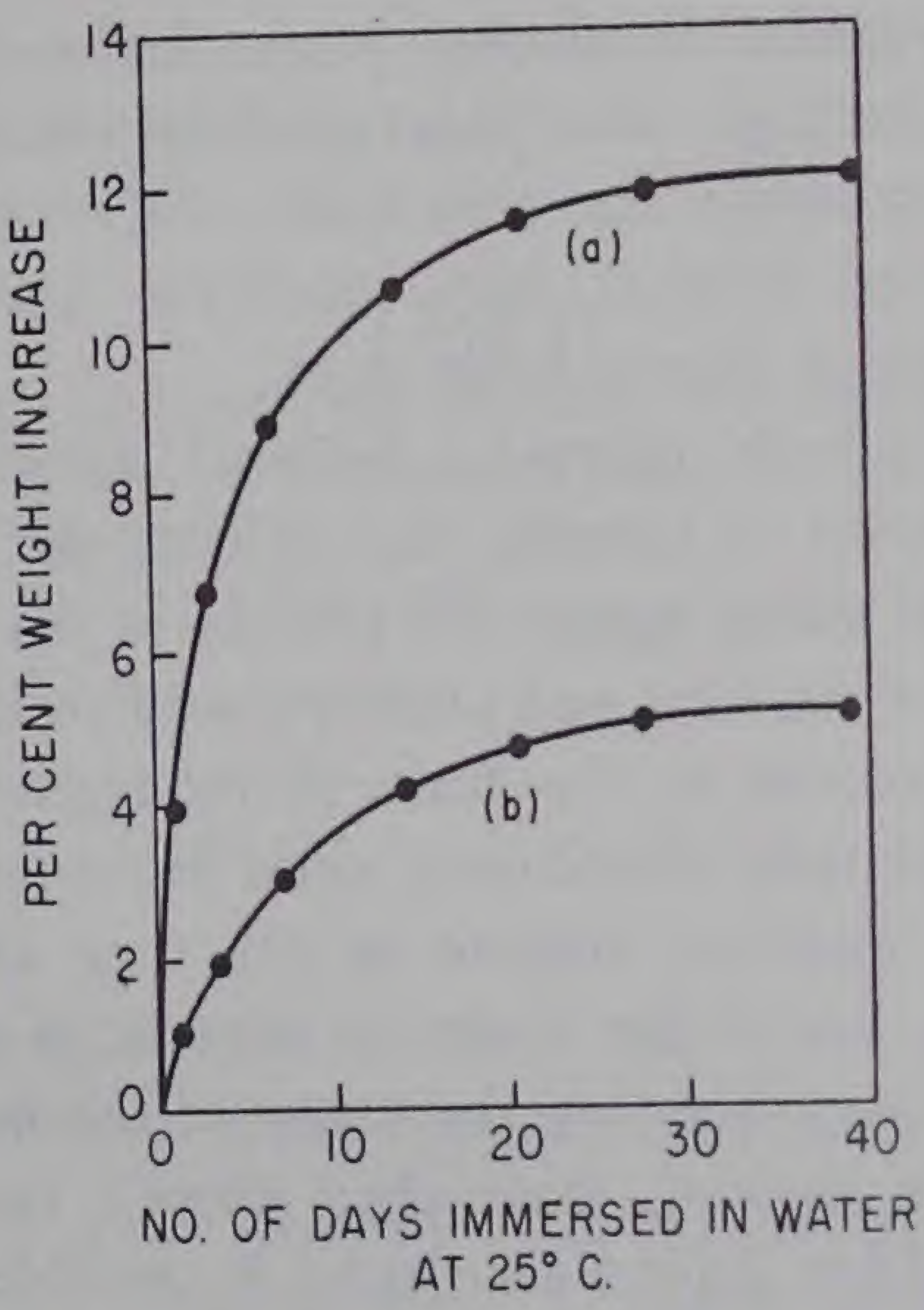

Fig. XXI-1. Effect of (a) solvent-soluble and (b) water-soluble phenolic resins on the water resistance of paper laminates.

Paper Used for Paper-Base Laminates. The tensile strength, stiffness, flexural, and impact strength of the laminated product are derived chiefly from the paper. The electrical properties of the laminate are also dependent upon the electrical properties of the paper, so that paper with low power factor, good dielectric strength, and high dielectric constant are required for electrical insulation work. However, the most important factor affecting electrical insulating properties is the amount of resin absorbed by the paper.

Paper for impregnating must be uniform. The paper should be free of fiber bundles and slime spots, since these resist penetration by the resin and tend to cause blisters in the laminated product. The finish should be low, since the adhesion between plies increases with increasing tooth on the paper. Thus, low-finish papers are used where a high degree of bonding between plies is necessary, for example, when the laminate is to be milled or drilled parallel to the laminations. High-finish paper may be desirable on the outside surface of the outside ply to increase the surface finish of the laminate, although this finish can be regulated during pressing.

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[38] G. A. Albert, *Paper Trade J. 101,* No. 11: 127–131 (Sept. 12, 1935)
[39] M. P. Seidel, *Tappi 32,* No. 8: 374–377 (Aug., 1949)
[40] H. Kline, *Paper Trade J. 119,* No. 13: 128–130 (Sept. 28, 1944)

The paper should have a *p*H around the neutral point, because too high a *p*H retards the curing of most resins, and too low a *p*H results in a brittle product. The paper should be free of bleach residues, since these reduce the electrical insulating properties and cause degradation of the paper during curing. The paper may be colored with direct dyes or a few selected members of the acid dyes. As a rule, however, colored pigments are preferred because they stand the heat of molding better and are more permanent than soluble dyes.

The paper is generally unsized. Internal sizing has relatively little effect on the penetration of varnish, but reduces the absorption of aqueous resin solution. If sizing agents are present in the original paper, they are decomposed under the heat and pressure used in lamination.

The moisture content at the time of impregnation should be low and the moisture uniformly distributed, since moisture affects the pick-up of varnish.[41] High moisture content at the time of molding improves the ease of molding, but if the moisture content is more than 4%, the dimensional stability and moisture resistance of the laminate are reduced.

Thin papers are desired, since they absorb resin more uniformly than thick papers. Thin papers also make it possible to obtain a higher degree of orientation if the sheets are cross-laminated. On the other hand, thick sheets produce laminates with greater tensile strength in the vertical direction, because of the greater number of fibers lying in a nearly upright position in thick papers.

The most important property of impregnating papers is the absorbency of the paper. High absorbency is desirable when good electrical resistance and minimum water absorption are required, because these properties depend upon the absorption of a high percentage of resin. On the other hand, when a laminated product of high impact strength and good punching qualities is desired, the paper should have a low absorbency to reduce the amount of absorbed resin. If a low percentage of resin is to be added, the sheet should have a high density so that all voids in the paper are filled. However, the density should not be so high that insufficient resin is added to meet the minimum water absorption requirements. Dickerman[42] gives 1.35 as the minimum specific gravity for a laminated product made from sulfite paper, since laminated products of lower specific gravity are lacking in compressive strength and water resistance.

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[41] A. H. Croup, *Paper Trade J. 118,* No. 20: 175–178 (May 18, 1944)

Almost all types of paper have been used in making paper laminates, but the most important are rag, kraft, sulfite, and alpha. Groundwood and soda pulps are too weak for general use. Kraft papers are used where strength is necessary and color is of no importance. Sulfite pulps of high alpha cellulose content are used where good electrical characteristics are desired or where the laminate is to be used for decorative purposes. Alpha pulps are used for maximum electrical resistance (e.g., radio insulation panels). Rag papers are used where minimum color is desired and where the laminated product must have excellent molding, machining, or punching qualities. As a rule, rag papers show better bonding between plies than sulfite or alpha papers.

TABLE II

WATER ABSORPTION OF LAMINATES MADE FROM VARIOUS TYPES OF PAPER
45% Phenolic Resin

Type paper	Water absorption[a]
0.005 Hard-finish kraft	5.7
0.009 Kraft	4.1
0.006 Sulfite	2.3
0.004 Alpha	1.7
0.004 Rag	1.3
0.010 Cotton linters	1.8

[a] Per cent gain on soaking twenty-four hours, sample 1 × 3 in.

Pitzer[43] lists the water absorption of laminates made from different papers containing 45% phenolic resin, as shown in Table II. These results show that kraft papers produce laminates of much higher water absorption than alpha paper, even when the same amount of resin is absorbed. Furthermore, kraft papers absorb less resin than rag and alpha paper for the same method of treatment, and this further increases the water absorption. Recently, however, kraft papers of greater absorptiveness have been produced. Dickerman[44] rates alpha, unbleached sulfite, and unbleached kraft as follows:

Property	Alpha	Sulfite unbleached	Kraft unbleached
Absorbency	1	3	2
Color stability	1	2	3
Electrical	1	3	2
Tensile	3	1	2
Toughness	2	3	1

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[42] G. K. Dickerman, *Paper Trade J. 118,* No. 26: 239–242 (June 29, 1944)

[43] J. C. Pitzer, *Tappi 32,* No. 8: 382–384 (Aug., 1949)

[44] Private communication from G. K. Dickerman

Two or more different grades of paper may be used in making a laminate. For example, a high-grade paper such as alpha or rag stock may be used as the top sheet and strong kraft used in the middle plies of decorative laminates.

Lamination and Molding. After being treated with resin, the sheet may be passed between squeeze rolls to drive the resin into the paper. In cases where maximum penetration is desired, the treated paper may be wound into rolls and allowed to stand before it is dried. This increases the time for penetration and allows the resin to become equalized in the sheet.

After impregnation, the paper must be dried to remove solvent. It is common practice to dry the sheet to an accurately controlled percentage of contained volatile matter. During drying, a partial polymerization of the resin occurs which serves to control the amount of resin flow in the subsequent molding stage. All thermosetting resins have a critical drying temperature beyond which they cannot be heated without prematurely curing the resin. The drying should not be so rapid that moisture is trapped within the sheet. After drying, the paper is ready for laminating or molding.

In making paper laminates, a number of sheets of resin-impregnated paper are placed in a pile and then laminated under heat and pressure. The number of sheets used depends upon the thickness required in the final laminate. The various plies are selected with an eye to the best utilization of raw materials. For example, it is common practice to use several layers impregnated with phenolic resin as the core of the laminate, and then to use paper impregnated with light-colored urea- (or melamine-) formaldehyde resin as the surface layer. A highly pigmented sheet may be used between the surface ply and the inner plies to prevent the dark-colored phenolic resin from bleeding through to the surface sheet. Pigmented sheets prevent show through in cases where the surface ply is fairly transparent.

The sheets may be cross-laminated by laying alternate sheets with their machine directions at right angles. Parallel laminated products show excellent strength in the machine direction, but tend to have low strength across the grain. Cross-laminated products have high strength in both the lengthwise and crosswise directions, although they have a slight weakness on the bias.[45] All laminates have a line of weakness between the plies, but in general, laminated plastics are mechanically stronger than pulp-filled plastics (described in the following section) because of the support furnished by the paper web. Seidel[45a] points out

[45] G. K. Dickerman, *Paper Trade J. 118*, No. 26: 239–242 (June 29, 1944)

[45a] M. P. Seidel, *Tappi 33*, No. 11: 549–551 (Nov., 1950)

that even with papers which have been made as free as possible of fiber orientation, there will be considerable orientation in the finished laminate, due probably to tension and compression exerted on the paper during the treating operation.

Laminating is done on large, hydraulic type presses equipped with steam-heated platens. If paper plastic tubes are to be made, the paper is wound into tube form and then is cured in an oven or on a mandrel under heat and pressure.

During the early stages of molding, the resin softens and flows, filling in the voids in the paper and bonding together the various plies. Upon further heating, the mass becomes relatively homogeneous, and the resin begins to polymerize and harden, growing from a product of low molecular weight to one of high molecular weight. The final polymerized resin is insoluble in water and is generally resistant to most chemicals. Undercuring results in poor adhesion between fibers and resin, and produces a laminate of low tensile strength. On the other hand, overcuring produces brittleness and results in a porous resin structure.[44] The effect of molding time on the water resistance of the laminate (measured by the per cent weight increase on soaking in water) is shown in Figure XXI-2, where it can be seen that overcuring results in a slight increase in water absorption.[44]

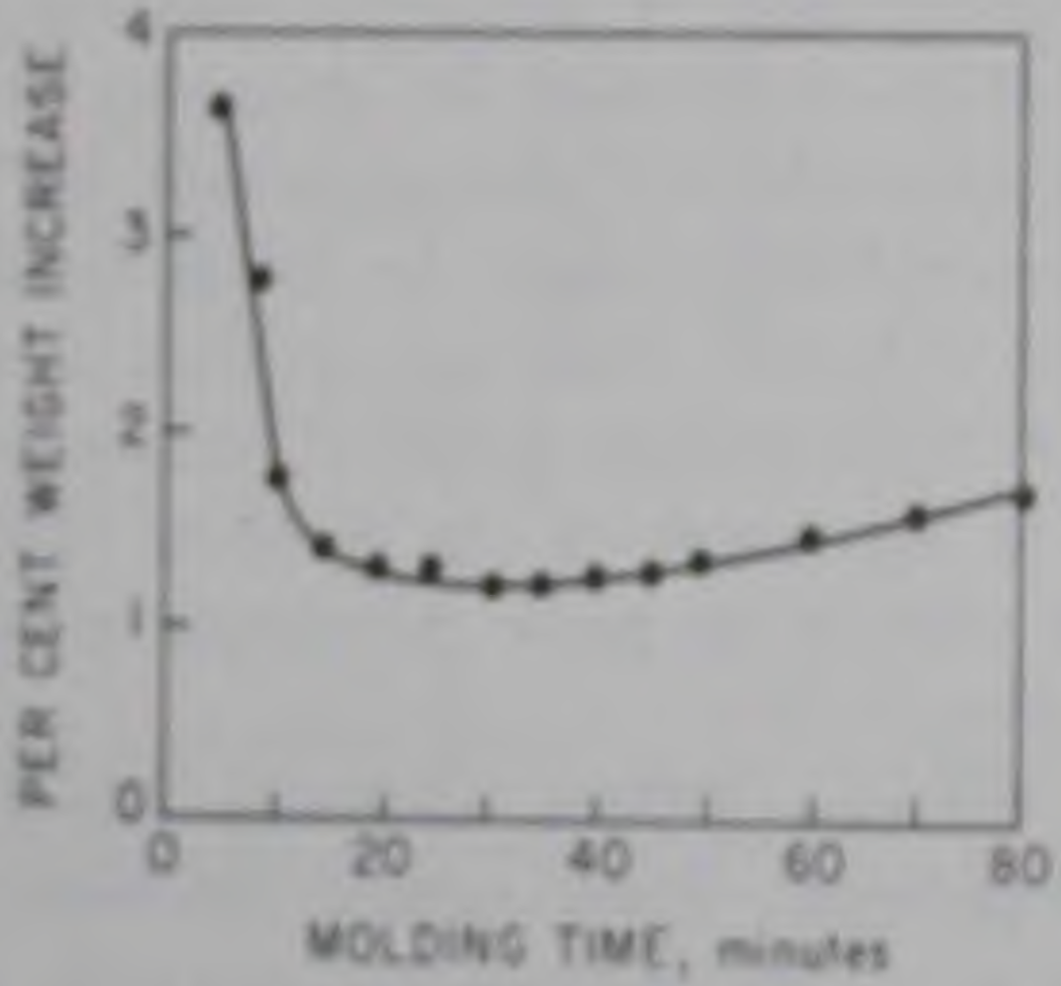

Fig. XXI-2. Effect of molding time on water absorption of paper laminates.

The molding and laminating characteristics depend upon the heat and pressure used and the type and amount of resin present in the paper. Increasing the amount of plastic material in the sheet reduces the amount of pressure required. However, the best all-round properties in the final laminate are obtained when there is just enough resin to fill all the voids in the sheet. More resin than this reduces the strength, whereas a lesser amount is not sufficient to impart the required water, chemical, or electrical resistance to the laminate. In some cases, more resin is used in the outer plies than in the inner plies. Increasing the amount of moisture in the sheet increases the flow of resin, but reduces the dimensional stability of the laminate.

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[44] C. J. Straka, *Paper Trade J.* 126, No. 14: 184-188 (Apr. 1, 1948)

The earliest laminating processes used high temperatures and relatively high pressures (1,000 p.s.i.). Since then, new resins have been introduced which can be laminated at lower pressures. In some cases, pressures as low as 50 p.s.i. can be used, although ordinarily pressures in low-pressure laminating run from 200 to 300 p.s.i. All the common thermosetting resins, including the urea-formaldehyde, melamine-formaldehyde, phenol-formaldehyde, and resorcinol-formaldehyde, can be molded under low pressure. Low-pressure laminating is popular because it permits molding of very large sheets.

Pulp-Reinforced Plastics

A pulp-reinforced plastic is a plastic molding composition which contains filler pulp added to increase the strength. A complete study of the properties of pulp-reinforced plastics would be far removed from papermaking and consequently cannot be taken up to any extent in a book devoted to that subject. However, neither should the subject be completely ignored, for the plastics industry consumes a large amount of pulp as an important ingredient of the molding composition. It is of interest to the pulp chemist to know something of the requirements of pulps used in this way.

Properties of Fibrous Fillers. Fibrous fillers perform a useful function in molded plastics. They extend the resin and improve the molding characteristics. They increase the strength, heat, chemical and electrical resistance of the molded product, lower the density, and improve the dimensional stability. Cellulose fillers absorb the moisture liberated by the resin during condensation, thereby swelling and offsetting the shrinkage of the resin.[47] If the cellulose did not swell in this way, the molded product would shrink and not conform to the mold dimensions.

Among the fillers commonly used are wood flour, cotton floc of various lengths, and chemical wood pulps such as sulfite, kraft, and alpha pulps. Wood flour of high quality is used for opaque moldings, whereas purified wood pulps or alpha cellulose are generally preferred for light-colored, translucent, or light-resistant molded products obtained from the molding of urea and melamine resins. Wood flour plastics excel in compressive strength and water resistance, but long-fibered stock is preferred for high shearing strength. Work at the Forest Products Laboratory[48] indicates that sulfate pulps and hardwood neutral sulfite pulps produce strong plastics, but groundwood pulp plastics are lacking in toughness, although still tougher than wood flour-filled plastics.

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[47] C. H. Pottenger, *Paper Trade J. 120*, No. 23: 225–227 (June 7, 1945)

Lewis and Ingle[49] give the following analytical constants for pulp suitable for molding: minimum alpha cellulose content of 85.5%, maximum pentosan content of 4%, maximum wood resin content of 0.2%, and a maximum solubility in 1% sodium hydroxide of 4%. The hemicellulose content should be held to a minimum, since hemicelluloses increase the water absorption of the molded product. Furthermore, hemicelluloses tend to cause yellowness in light-colored urea-formaldehyde plastics.[50] Resins and tannins are undesirable because they lower the color, especially if solvents are used in which the resins are soluble.

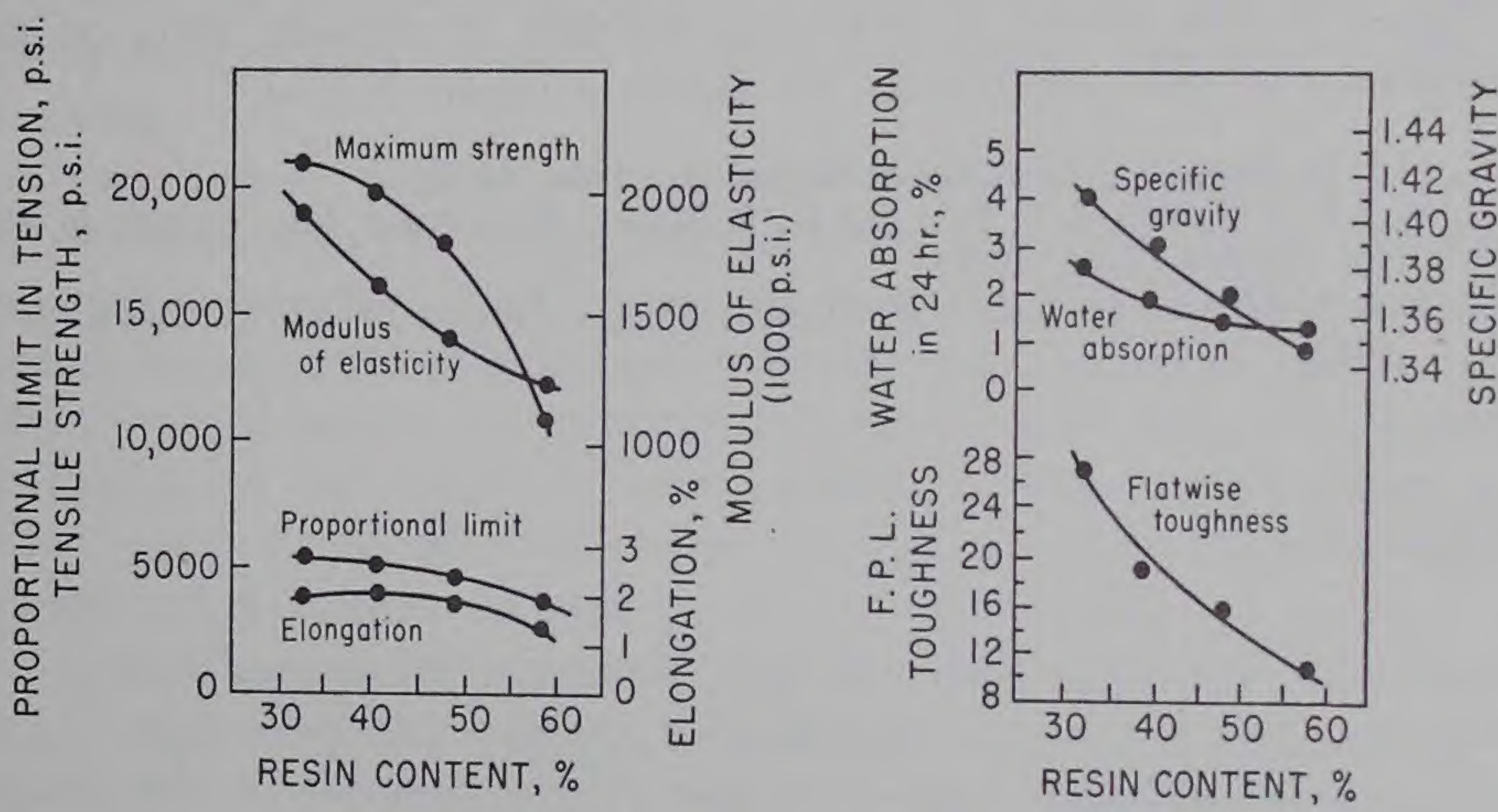

Fig. XXI-3. Effect of amount of phenolic resin on properties of kraft-filled plastics.

High lignin content is undesirable in pulps for light-colored molded products, but not objectionable in dark-colored products. Lignin functions as a thermoplastic resin, but it has a lower heat resistance and a higher water absorption than phenolic resins. One process calls for enrichment of filler pulp with lignin obtained from waste cooking liquor.

Effect of Resins. The resin may be added to filler pulp as a dry powder or as a varnish. After the resin is thoroughly mixed with the fiber, the product is ready for molding. In one process, alpha cellulose is impregnated with an aqueous solution of urea-formaldehyde resin, dried in vacuum, mixed with coloring agents, and then blended with the resin and other ingredients.[51] The resulting composition can be molded at a temperature of about 140° C. and a pressure of 3,000 to 6,000 p.s.i. to produce a translucent product.

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[48] S. L. Schwartz, J. C. Pew and H. R. Meyer, *Pulp Paper Mag. Canada 46,* No. 10: 771–779 (Sept., 1945)

[49] G. H. Ingle and H. F. Lewis, *Paper Trade J. 113,* No. 8: 91–94 (Aug. 21, 1941)

[50] *Idem.*

Increasing the resin content of the molding composition decreases the pressure required in molding. However, excessively high resin content is likely to result in resin pockets in the final product. In most cases, the resin content varies from 35 to 50% of the weight of the molding composition.

The resin acts as the principal bonding agent. Fiber-to-fiber bonding is only of minor importance; beating the pulp actually decreases the tensile strength of the molded product.[52] Increasing resin content reduces water absorption, but also tends to reduce the toughness and strength of the plastic, although tensile strength is not always adversely affected.[53] The effects of increasing amounts of phenolic resin on the properties of kraft pulp plastics are shown in Figure XXI-3.[52]

[51] J. D. Morgan, *Paper-Maker* Annual No. 1946: 17–18

[52] S. L. Schwartz, J. C. Pew and H. R. Meyer, *Pulp Paper Mag. Canada 46*, No. 10: 771–779 (Sept., 1945)

[53] R. U. Hanslanger and R. H. Mosher, *Modern Plastics 20*, No. 11: 76–79 (July, 1943)

CHAPTER XXII

COATING WITH RESINOUS MATERIALS

This chapter is concerned with coated papers, particularly those papers coated with resinous materials. These papers are made by applying a fluid mixture of resinous coating compound to the surface of the paper and then drying. The base paper may be either supercalendered sulfite, kraft, glassine, or cellophane. The coating mixture may be either a lacquer, an aqueous dispersion, an emulsion, latex, organosol, plastisol, or a hot melt. Cellophane and glassine make ideal base stocks because their smooth, nonporous surface makes it possible to obtain good results with small amounts of coating.

Papers coated with resins are used primarily for wrapping and packaging where the function of the paper is to protect the contents. Coated wrapping papers have many advantages over uncoated wrapping papers, because several different functional properties can be combined in a single sheet of coated paper. For example, uncoated glassine has good physical strength and a high degree of water resistance, but it is not resistant to water vapor. Coated glassine has the desirable properties of the uncoated product and, in addition, is quite resistant to water vapor.

Coated papers are sometimes used for their improved appearance (e.g., coated fancy box papers). These papers belong in the protective coating field for two reasons: (*1*) because the same materials and processes are used, and (*2*) because one purpose of the coating is to protect the paper from soil. In many cases, the coating is both protective and decorative, as in the case of cartons, labels, shelf paper, lamp shade stock, and bottle-cap stock, where the coating is primarily protective but also serves a decorative purpose. Some coatings are purely protective, for example, coatings applied to the inside surface of paper cartons to prevent the loss of moisture and essential aromatic compounds and to retain the crispness, firmness, and other qualities of the packaged product. The various reasons for coating paper with resinous materials may be summed up as follows: (*1*) to improve the decorative value, (*2*) to provide protection against oils, greases, water, water vapor, gases, chemicals, solvents, abrasion, and heat, (*3*) to provide heat- or pressure-sealable coatings for sealing tapes, bread wrappers, gaskets, etc., and (*4*) to provide electrical insulation.

Some of the general properties required in wrapping papers are high strength (particularly resistance to tear and puncture), good creasing qualities (particularly when used on automatic machines), good color, cleanliness, a high degree of resistance to the penetration of liquid and gaseous materials, good printing qualities, and good aging properties. If the wrapper must stand stretching, creped paper may work best.

Before starting this chapter, the reader is informed that there is a subsequent chapter on the properties of resins. The properties of resins are discussed in a separate chapter because of the multiple uses of resins in such operations as coating, impregnating, laminating, and saturating, which makes it impossible to assign a particular resin to any one chapter. Furthermore, the number of resins being used is so great that a description of each resin in a chapter on coating, for example, would make that chapter far too bulky. The rule which has been followed has been to discuss the general properties of resins in the chapter on properties of resins, and to discuss the more specific properties in the chapter pertaining to the use of these materials.

Fundamental Properties of Films

Success in protective coating depends upon the ability to produce a satisfactory film of resinous or waxy material on the surface of the paper. The coating must meet the following requirements: good adhesion, freedom from tackiness, freedom from blocking, good flexibility, freedom from color and odor, freedom from toxicity, high gloss, resistance to deterioration on aging, resistance to water, oils, water vapor, etc., and good heat seal.

Adhesion of Films

The coating must adhere strongly to the base paper. Adhesion is particularly important if the coating is to be heat-sealed.

Most resins adhere fairly well to paper, but may not adhere so well to cellophane and other smooth materials. The degree of adhesion depends upon the type and magnitude of the bonding forces between the coating and the paper surface. The attractive forces which may be involved in order of increasing magnitude are mechanical bonding, dipolar bonding, hydrogen bonding, and covalent bonding. Polar resins have a high degree of specific adhesion for cellulose, whereas non-polar resins are dependent upon mechanical adhesion. According to McLaren and Hofrichter,[1] the order of increasing adhesion which various substituent groups exhibit for cellulose is as follows: alkyl, nitrile, chloromethylene, dichloromethylene, butyral, and hydroxyl. They found poor adhesion to exist between cellulose and rubber, polyethylene, cellulose acetate, ethylcellulose, polyvinyl chloride, and polystyrene. Adhesion was good between cellulose and polyisobutylene, and nitrocellulose, and excellent between cellulose, polyvinyl alcohol, the urea- and melamine-formaldehyde resins, and the phenolics. Adhesion of resinous coatings for paper can be improved by saturating the paper with rubber or resin emulsions.

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[1] A. D. McLaren and C. H. Hofrichter, *Paper Trade J. 125,* No. 19: 96–100 (Nov. 7, 1947)

Another method of obtaining satisfactory adhesion between cellulose and a material which normally will not adhere to cellulose is to precoat the paper with a substance which is adherent to both the paper and the second coating. Cheyney[2] has patented a process of precoating paper with polyvinyl chloride and then overcoating with vinylidene chloride.

Adhesion takes place in two stages: (*1*) migration or movement of the polymer to the interface and (*2*) sorption of the polymer at the interface of the paper. The degree of adhesion is related to the average molecular weight and chain length of the resin,[3] a degree of polymerization in the neighborhood of 50 to 300 being most effective.[4] According to McLaren,[5] the lower the tack temperature of the resin,, the better the adhesion. The density, strengh, and adhesion of resinous films can often be improved by heating the coated paper.[6]

Film Flexibility

The continuity of the film is an important factor when coated papers are used for protective purposes, e.g., as wrapping or shelf papers. If the film is cracked or checked, it will not be effective in holding back water, gases, or oils. Resins are commonly classified as film-forming or non-film-forming.

The important property is the degree of film continuity after the coated paper has been put to use, which usually means after it has been subjected to a considerable amount of handling. Many coated papers are used under conditions where they are flexed and creased many times during their life. Sometimes flexing takes place at relatively low temperatures, e.g., as in wrappers for frozen foods. The question of flexibility is of great importance when the coated paper is used on automatic wrapping machines. An important factor is the amount of plasticizer in the film. The thickness of the film is also important, since thin films are more flexible than thick films. The effect of aging on film flexibility is important, particularly when plasticizers are used in the coating.

No method of testing film flexibility is completely satisfactory. One simple method involves creasing the paper in a creasing device and then smearing the coating with a penetrating substance, such as water or oil con-

[2] L. V. E. Cheyney, U. S. 2,392,972 (Jan. 15. 1946)

[3] C. H. Young, G. W. Gebhardt, W. K. Schneider and G. W. Seagren, *Ind. Eng. Chem. 33*, No. 1: 72–74 (Jan., 1941)

[4] H. Mark, *Physical Chemistry of High Polymeric Material,* Interscience Publishers. Inc., New York, N. Y. (1940)

[5] A. D. McLaren, *Paper Trade J. 126,* No. 22: 263–264 (May 27, 1948)

[6] H. L. Bender, *Ind. Eng. Chem. 29,* No. 11: 1130–1134 (Oct., 1937)

taining a soluble dye, to see if any penetration takes place at the creases. The humidity at which the paper is conditioned has an important effect on the test results.

Hardness of Films

Most resinous materials exhibit a transition point at which the material changes from a hard substance to a soft, sticky substance. This is known as the softening point. The softening points of some of the common resins are listed below. The three-dimensional resin polymers do not exhibit a softening point.

Non-film-forming resins	Softening temperature
Shellac	70–80° C.
Dammar	65–70° C.
Manila	70–90° C.
Kauri	90–125° C.
Rosin	80–85° C.

Film-forming resins	Softening temperature
Cellulose acetate	220–250° C.
Cellulose acetate butyrate	205–225° C.
Ethylcellulose	165–200° C.
Polyvinyl acetate	45–85° C.
Cyclized rubber	50–75° C.

In substituted products, the softness depends upon the substituting agent and the degree of substitution. Cellulose propionate produces a softer film than cellulose acetate. Ethylcellulose has its minimum softening point at a degree of substitution of about 2.4. Asphalts, the higher alkyl molecular weight acrylic and methacrylic resins, and certain other resins have too low a softening point to be used as surface coatings by themselves.

Film hardness is related to the durability of the coating. Durability can be measured by a special abrader equipped with different abrasive surfaces and a numerical counter to record the number of rubs. The scuff resistance is measured by (*1*) the number of rubs for complete disruption of the coating, or (*2*) the reduction in gloss obtained after a definite number of rubs.

Blocking. If the coating is too soft, it exhibits a condition known as blocking, in which adjacent coated surfaces unite under heat and pressure so that the film continuity and gloss are destroyed. Blocking occurs when the coated paper is stacked in piles. It also occurs in paper wound tightly into rolls when thermal expansion sets up internal pressure in the roll.

Blocking can be determined in the laboratory by subjecting a stack of coated sheets to a definite pressure and temperature. One method calls for stacking twelve sheets of the test specimen between two pieces of plate glass under a pressure of 1 p.s.i. for twenty-four to seventy-two hours. The sheets can be placed in desiccators maintained at constant relative humidity and the whole assembly placed in an oven maintained at a temperature below the softening point of the coating. The results are reported as: (*1*) no blocking, if the coating retains its gloss and the sheets slide readily over each other; (*2*) slight blocking, if the sheets do not slide readily; (*3*) complete blocking, if the surface of the coating is marred, or if the coating pulls fibers, or if a complete seal is formed. Most coatings are formulated to be non-blocking at 125 to 130° F. If the coating does not meet this requirement, it must be reformulated, or it can be dusted with starch, talc, or mica to prevent blocking.

Heat Seal. For certain purposes, coated papers must have heat-sealing properties. Packaging papers are frequently heat sealed by heating two plies of the coated paper with a hot iron for a few seconds at a temperature of about 275 to 350° F. The coatings should fuse and form a strong bond under these conditions. Heat-seal adhesives are discussed in Chapter XX.

Slippage. Another important property required in certain coatings is slippage, or the ability of the coating to slip over hot metal surfaces. Slippage is sometimes imparted to the coating by adding paraffin wax to the coating formula.

Gloss

Gloss is important wherever the coating is used for its decorative effect. Gloss is particularly important in overprint varnishes for labels, covers, etc. On the other hand, gloss is relatively unimportant in wrapping papers. Gloss is obtained by the use of the proper resins in the coating. Coated papers can be given a numerical rating for gloss by comparing to a standard of 100 obtained by covering a sample of the uncoated paper with a piece of plate glass.

Gas Permeability of Coated Papers

Many articles are susceptible to oxygen and must be sold in packages having a low degree of gas permeability. Coffee, for example, is deteriorated by oxygen and should be packaged in containers permitting the entry of less than 3 cc. of oxygen per 100 g. of coffee.[7] Wrappers for certain polished metallic articles should have a low permeability to oxygen in order to reduce corrosion of the metal. In packaging tea, butter, shortening, and starch, wrappers must be chosen which are impervious to gases in order to prevent the absorption of foreign odors. Spices must be packaged in such a way as to retain the volatile odors and essential oils, which are a valuable part of the product. On the other hand, some gas permeability is desirable in wrappers for cheese in order to permit the passage of carbon dioxide liberated by the cheese.

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[7] L. C. Cartwright, *Paper Trade J. 124*, No. 25: 275–277 (June 19, 1947)

Gases penetrate through films by one or both of the following methods: (*1*) pore type penetration and (*2*) solution permeation (whereby the gas dissolves in the sheet, diffuses through, and evaporates at the other side). Pore type penetration is a factor once the gas reaches the fibrous part of the coated paper, but is of relatively little importance in the penetration of surface films.

Permeability depends upon the type of gas and the temperature. Davis[8] found that the permeability is highest with carbon dioxide and decreases in the following order: carbon dioxide → oxygen → nitrogen. This is the reverse of that expected from Graham's law, but can be explained by differences in the resonating nature of the gases.

Gas permeability can be measured by using the specimen as a barrier and applying pressure to one side. The gas then permeates from the high-pressure to the low-pressure side, thus changing the pressure of the gas. Either the change in volume or the change in pressure of the gas can be measured. Increasing the applied pressure results in a great increase in the rate of transmission if the penetration is principally through the pores of the paper. On the other hand, increasing the applied pressure does not change the rate of penetration to so great an extent if solution permeation is involved.

Davis[9] has described another slightly different method for measuring permeability in which two or more gases are used, so that the total pressure is equal on both sides of the test sheet. The proportion of gases is regulated to maintain a significant difference in the partial pressures between the two sides of the sheet.

Water-Vapor Resistance

Water-vapor permeability is a special case of gas permeability. It is defined as the weight of water vapor passing through the specimen per unit of area and unit of time, and at some fixed temperature and vapor pressure differential.

High water-vapor resistance is required in packages containing cement, flour, cereals, salt, and other materials which tend to cake and harden in the presence of excess moisture. Metal parts and packaged chemicals are other materials which must be protected from the damaging effects of water vapor. Popcorn, tobacco, bread, and frozen meats are examples of products which must be packaged in water vaporproof packages in order to prevent loss of moisture from the product.

No direct relation exists between the air permeability of paper and the water-vapor resistance.[10] Furthermore, there is no relation between the water-vapor resistance and the sizing. The lack of correlation between sizing and water-vapor transmission can be explained by the fact that liquid water passes through the pores of the paper, whereas water vapor is transmitted through the fibers, as well as through the interfiber pores. Paper can be sized against liquid water (*1*) by coating the individual fibers with a substance which lowers the contact angle with water (e.g., rosin) or (*2*) by filling in the pores of the sheet with some hydrophobic substance (e.g., wax). However, these methods do not appreciably increase the water-vapor resistance of the paper. The only means by which the paper can be made water vaporproof is by coating the surface of the paper with a continuous film of a hydrophobic substance (wax, rubber, etc.) which completely covers the surface of the sheet, as well as any fibers protruding above the surface.

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[8] D. W. Davis, *Paper Trade J. 123,* No. 9: 97–104 (Aug. 29, 1946)

[9] *Idem.*

The above explains why a paper which has been surface-coated with wax will be relatively water vaporproof, whereas a sheet impregnated with wax will not. It further explains why a paper which has been impregnated with wax will absorb nearly as much water as an unimpregnated paper (although the rate of absorption will be lower) unless a surface film of wax is present. Water which comes into contact with one part of a sheet will, in time, become uniformly distributed throughout the rest of the sheet. Consequently, if moisture should pass through a break in the surface coating, it will spread throughout the entire sheet. This makes it necessary to maintain a continuous surface film of protective coating, because otherwise the protective qualities will be lost.

Moisture appears to move through surface films in the condensed state, i.e., as moisture having a density approaching that of liquid water.[11] Solution permeation plays an important role, i.e., the water dissolves in the surface film of coating material and passes between the individual molecules until it reaches the other side of the film. In severe cases, the presence of water causes whitening of the film, resulting in a spongy, porous film. Because of solution permeation, a film may not be resistant to water vapor, even though it is impervious to air.

The transmission of water vapor is directly proportional to the area exposed and the time of exposure. For homogeneous plastics, the amount of water passing through the film is inversely proportional to the thickness of the film.[12,13] Even with coated papers, there appears to be a linear relationship between the thickness of the coating and the resistance to vapor transmission.[14]

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[10] A. Abrams and W. A. Chilson, *Paper Trade J. 91,* No. 18: 175–180 (Oct. 30, 1930)

[11] F. T. Carson, *Paper Trade J. 125,* No. 19: 118–128 (Nov. 7, 1947)

[12] P. M. Doty, W. H. Aiken and H. Mark, *Ind. Eng. Chem., Anal. Ed. 16,* No. 11: 686–690 (Nov., 1944)

[13] C. L. Comar and E. J. Miller, *Ind. Eng. Chem., Anal. Ed. 15,* No. 12: 737–740 (Dec., 15, 1943)

A predominant factor influencing water-vapor transfer is the relative humidity of the air.[15] An increase in humidity on one side of the sheet results in a rapid increase in the transmission rate. The effect of humidity is particularly great on films of high water absorption. Some films which are highly vaporproof under ordinary conditions show a high rate of transmission at high humidities. These films absorb water in equilibrium with the air on the high humidity side of the sheet, and not with the average of the two sides.[16] On the other hand, films of low water absorption (e.g., polyethylene) show a uniform variation in moisture content throughout the film,[17] and hence are less affected by changes in relative humidity. Under certain circumstances, permeability is directly proportional to the vapor pressure difference across the film,[18, 19] but this relationship does not always hold throughout the complete range of humidity.[20, 21] Church and Scroggie[22] found a direct relationship between permeability and vapor pressure differential below a relative humidity of 75%. When relative humidity is constant and temperature variable, permeability is directly proportional to vapor pressure differential. However, when temperature is constant and relative humidity variable, the relationship between permeability and vapor pressure difference is often not a direct one.

In general, permeability increases with increased temperature, because the vapor pressure difference is increased at higher temperatures. Conversely, a reduction in temperature causes a reduction in vapor transmission. Theoretically, a plot of vapor transmission rate against the reciprocal of the absolute temperature should be a straight line.[23] Aiken[24] found that the rate of transmission of water vapor through uncoated cellophane at 0° F. is about 1/51 of the rate at 100° F. High temperatures affect transmission rate by softening the coating, particularly when low-melting-point materials, e.g., paraffin, are used.

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[14] H. J. Wing, *Ind. Eng. Chem. 28*, No. 7: 786-788 (July, 1936)

[15] W. H. Aiken, *Paper Trade J. 125*, No. 14: 153-157 (Oct. 2, 1947)

[16] A. Abrams and G. J. Brabender, *Paper Trade J. 102*, No. 15: 204-213 (Apr. 9, 1936)

[17] Discussion *Tappi 32*, No. 5: 202 (May, 1949)

[18] P. M. Doty, W. H. Aiken and H. Mark, *Ind. Eng. Chem., Anal. Ed. 16*, No. 11: 686-690 (Nov., 1944)

[19] C. L. Comar and E. J. Miller, *Ind. Eng. Chem., Anal. Ed. 15*, No. 12: 737-740 (Dec. 15, 1943)

[20] W. H. Church and A. G. Scroggie, *Paper Trade J. 101*, No. 14: 200-209 (Oct. 3, 1935)

[21] R. L. Taylor, D. B. Herrmann and A. R. Kemp, *Ind. Eng. Chem. 28*, No. 11: 1255-1263 (Nov., 1936)

[22] W. H. Church and A. G. Scroggie, *Paper Trade J. 101*, No. 14: 201-209 (Oct. 3, 1937)

[23] P. M. Doty, W. H. Aiken and H. Mark, *Ind. Eng Chem. 38*, No. 8: 788-791 (Aug., 1946)

[24] W. H. Aiken, *Paper Trade J. 125*, No. 14: 153-157 (Oct. 2, 1947)

There are numerous methods for measuring water vapor permeability of paper and paperboard products. In one method, a sample of the test material of known area is clamped over the top of a small container which is partially filled with water or a saturated salt solution. The specimen is sealed to the rim of the container, using a mixture of paraffin and microcrystalline wax to make a vapor-tight seal. The assembly is placed in a cabinet under controlled humidity and air circulation, and left there for a specified length of time, usually twenty-four hours. The loss in weight is determined and reported as the grams of water vapor per 100 sq.in. or per square meter of surface per twenty-four hours. In a variation of this method, the container is filled with a desiccant, e.g., anhydrous magnesium perchlorate, and the assembly is placed in a cabinet or room maintained at a relative humidity of 50% and a temperature of 73° F. In this case, the gain in weight is reported. In a statistical study of this method, Renner[25] found that the greatest source of variability in results is assignable to the day on which the samples are tested and the position of the samples in the test cabinet.

Pierce and Helms[26] describe a variation of the above method. In their method, the assembly is sealed in an impermeable cell and stored at the proper temperature while a controlled current of dried gas is passed through the cell to remove the water vapor escaping from the assembly. The escaping water vapor is absorbed by a desiccant which is weighed at frequent intervals.

Most of the methods used for measuring water-vapor permeability are based upon a gravimetric measurement of the gain or loss of water. This is very slow, because enough time must elapse to result in the transfer of sufficient water to cause an appreciable change in weight. Van den Akker[27] describes two methods using an electric hygrometer for measuring the change in relative humidity resulting from the transfer of moisture. The first method, called the dynamic method, involves the passage of dry air of known relative humidity over one side of the test sheet while the sheet is held in a diffusion cell under carefully controlled conditions of temperature and humidity. The relative humidity below the test sheet is maintained at a constant high value by means of a saturated salt solution. The relative humidity of the air passing over the top of the sheet is measured at regular intervals and plotted against time. The *initial* rate of change is taken as an indication of the water-vapor permeability, and because this method does not call for equilibrium, the method is very rapid. According

[25] M. S. Renner, *Paper Trade J. 125*, No. 6: 65-68 (Aug. 7, 1947)
[26] S. W. Pierce and J. F. Helms, *Paper Trade J. 124*, No. 16: 64 (Apr. 17, 1947)
[27] J. A. Van den Akker, *Paper Trade J. 126*, No. 1: 6-10 (Jan. 1, 1948)

to Van den Akker,[28] this method can be used for determining water-vapor permeabilities as low as 0.001 g./100 sq.in./day (at 0° F. and a relative humidity differential of 73%) in from four to five hours. This method is suitable only for the testing of relatively non-hygroscopic films.

In the second method, called the sweep-gas method, dry air of known initial humidity and known rate of flow is swept over the upper surface of the sheet. The air in the compartment below the sheet is maintained at a definite high value by means of a saturated salt solution. This method is based upon the principle that the air leaving the upper compartment changes in relative humidity according to the volume rate of air flow, the permeability of the specimen, the area of specimen, and the initial relative humidity of the entering air. The volume rate of flow of air in the upper chamber is regulated so that the relative humidity of the air leaving this chamber is carefully maintained about 3% higher than that of the incoming air. This difference in humidity is accurately determined by an electric hygrometer. The water vapor permeability is determined as follows:[29]

$$\text{W.V.P.} = K(r_2 - r_1)pQ$$

where K is a constant, r_2 is the relative humidity of air leaving the chamber, r_1 is the relative humidity of air entering the chamber, p is the density of saturated water vapor at the temperature used, and Q is the volume rate of flow of air over the specimen. This method is an equilibrium (steady-state) method, and consequently is more time-consuming than the dynamic method. It is, however, free from errors due to sorption phenomena.

In testing heavy boards, the absorptiveness of the paper must be taken into account. If the paper is highly absorptive, it tends to lower the humidity of the air on the high humidity side of the test. Sufficient time must be allowed for the transmission rate to come to equilibrium. In order to determine when a steady rate of transmission has been reached, the rate values should be plotted against time until a constant slope is obtained. A steady rate of moisture transmission may not be reached in some cases for two to three weeks.[30] In some cases, the permeability increases with time,[31] and consequently the test should not be run so long that a change is brought about in the material being tested. The sheet should be exposed in the test apparatus in the same manner as it will be exposed in use, e.g., a sheet designed for packaging dry products should be tested with the inner surface exposed to the low humidity side of the testing apparatus. The utility of packaging materials depends upon their ability to retain their water-vapor resistance upon creasing. Most permeability tests are made on flat sheets. However, a comparison of values made on papers creased in a special creasing platen with values obtained on flat sheets gives a useful indication of the effect of creasing on water-vapor resistance.

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[28] J. A. Van den Akker, *Paper Trade J. 126*, No. 1: 6–10 (Jan. 1, 1948)

[29] W. A. Wink and L. R. Dearth, *Tappi 32*, No. 5: 232–238 (May, 1949)

[30] G. J. Brabender, *Paper Trade J. 119*, No. 16: 160–163 (Oct. 19, 1944)

[31] F. T. Carson, *Paper Trade J. 125*, No. 19: 118–128 (Nov. 7, 1947)

Coating materials differ widely in their water-vapor resistance. When the General Foods test cabinet is used, the permeability is considered to be low if 0.15 g. or less of water vapor is transmitted, while the permeability is considered to be high if over 1.00 g. of water vapor is transmitted per 100 sq.in. per twenty-four hours. Cyclized rubber, polyethylene, nitrocellulose-wax combinations, vinylidene chloride copolymers, and certain of the synthetic rubbers are some of the materials noted for producing highly water-vapor resistant coatings. Pierce and Helms[32] obtained the values in Table I showing the relative rates of transmission of water vapor at 0° F. for several different packaging materials. Such low temperature comparisons are useful for frozen food wrappers. Metal foils have the greatest water-vapor resistance, but even they are not absolutely resistant to the penetration of water vapor under all conditions.

TABLE I

WATER-VAPOR TRANSMISSION OF SEVERAL PACKAGING MATERIALS

Material	Gain, g./100 sq.in./24 hr.
0.017 Paperboard	0.907
0.0018 Waxed paper (creased)	0.317
0.0018 Waxed paper	0.042
Rubber hydrochloride film	0.016
0.00035 Aluminum foil	0.012
0.017 Paperboard (wax-coated)	0.004
0.0009 Moistureproof regenerated cellulose	0.003
0.0007 Aluminum foil	0.000

Machinery for Coating with Resins

Many different types of coating machines are used for applying plastic coatings. Three important types of coaters, knife, roll, and air, are described below.[33]

Knife Coaters

Knife coaters are of several types, commonly called the floating knife coater, the blanket type knife coater, and the rubber spreader. These vary principally in the way in which the paper web is supported, but they all use a knife for spreading the coating on the paper. The larger the radius of the knife, the greater the amount of coating which is applied. The paper should leave tangent to the radius of the knife and perpendicular to the cut of the knife. The angle of the knife should be inclined from the vertical in the direction of web travel. A disadvantage of knife coaters is their tendency to cause streaks when particles become lodged under the knife. The knife used may be a solid knife or the Mayer-type applicator with a revolving wire-covered rod at the apex of the knife.

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[32] S. W. Pierce and J. F. Helms, *Paper Trade J. 124,* No. 16: 174–176 (Apr. 17, 1947)

[33] The description is taken in part from a talk given by M. A. Gaio of John Waldron Corporation, New Brunswick, N. J., Aug. 16, 17, 1948, before the Plastic Conference of TAPPI

In the floating knife coater, the coating is applied onto the face of the paper in front of the knife. The thickness of the coating is controlled by the angle of the knife, radius of the knife, and tension on the web. The paper is unsupported, and hence only heavy papers can be coated by this method. Dams are used to keep the coating on the paper.

The blanket type knife coater uses a rubber blanket as a support for the paper web and the knife. Weak papers can be coated by this method better than by the floating knife because of the support furnished to the paper by the rubber blanket. More uniform coatings are also obtained because of the more uniform tension supplied by the blanket.

The rubber spreader employs a knife mounted above a rubber roll. The rubber roll furnishes uniform pressure on the web against the knife.

Roll Coaters

There are a large number of roll coaters, some of the more important of which are mentioned below.

The *doctor kiss roll* is one type of roll coater. It employs an applicator roll and a knife for removing excess coating. This type of coater is used on low solids, low-viscosity coatings.

The *roll kiss coater* uses two rolls, a furnish roll revolving in the coating mixture and an applicator roll directly above. The paper is passed over the top (applicator) roll.

The *pressure roll coater* uses two rolls, an applicator roll and a backing roll. The paper is passed between the two rolls. The large ribs produced in the coating by this type of coater can be reduced in size by passing the paper over a smaller smoothing roll. If two-side coating is desired, a pipe can be used for applying coating to the top side of the paper.

The *reverse roll coater* employs three rolls, a doctor roll, a polished metal casting roll, and a rubber-covered backing roll. The paper passes between the casting roll and the backing roll under slight pressure. The amount of coating applied is governed by the opening between the doctor and casting rolls and the speed of the casting roll in relation to the web speed. It has been shown, in the case of a laboratory reverse roll coater, that the wet thickness (t) of the film applied is determined by the following relationship:[34]

$$t = kDR$$

where D is the doctor roll clearance, R is the ratio of speeds of casting roll to backing roll, and k is a constant. The thickness is independent of web speed so long as R, the ratio of casting roll to backing roll speeds, remains constant. Any decrease in casting roll speed below a critical value of R (a value less than 1) results in an irregular coating. This coater will handle a wide range of coating viscosities and is particularly applicable for viscous coatings.

Air Knife Coater

In this type of coater, the coating is applied to the web in excess by means of a coating roll. A slotted air blade is then used for distributing the coating and blowing off the excess. The air slot can be adjusted for width, for angular position, and for position in relation to the backing roll. The thickness of the coating depends upon the amount of coating applied and the amount removed, the latter being controlled by changing the air pressure.

Coating with Lacquers

Lacquers consist of a resin dissolved in a suitable solvent, e.g., shellac dissolved in alcohol, although commercial lacquers are generally more complicated than this. A typical composition consists of a film-forming resin dissolved in a suitable solvent, a plasticizer to make the film flexible, and a non-film-forming resin to increase the hardness and gloss of the film. Because a high percentage of solvent is used, lacquers are sometimes referred to as solvent coatings. Lacquers frequently contain dyestuffs, pigments, or metallic powders. Coatings for heat-sensitive record papers contain special salts which react to produce fine black lines on the coating when written upon with a heated needle.

Solvent coatings are used for decorative wrappers, food wrappers, and bottle-cap linings. They may be applied as overprint varnishes. Coatings can be produced which are water-resistant, water-vapor resistant, grease-resistant, alkali-resistant, and heat-sealing by proper formulation of resin, plasticizer, and solvent.

Solvent coatings produce dense films, are easy to apply, and are quickly dried, even in heavy films. Most of the common resins can be applied in solvent form, which is not true of other methods of application. On the other hand, solvent coatings create a fire hazard, and are expensive to use, unless equipment is available for recovering the solvent. Other disadvantages are that bubble-free coatings are difficult to obtain in heavy coatings, and solvent retention may cause trouble with undesirable odors in the finished product.

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[34] G. Broughton, L. W. Egan and R. C. Sturken, paper presented at 35th Annual Meeting of TAPPI, New York City (Feb. 20–23, 1950)

Methods of Applying Solvent Coatings

Solvent coatings can be applied by roll coaters, spray coaters, dip coaters, and knife coaters. Drying is very rapid (1–2 minutes) and can be done in conventional type ovens, radiant transfer ovens, or indirect fuel heaters. Drying temperatures vary with the type of lacquer. Certain of the thermoplastic resins have a minimum drying temperature below which the coating will show poor adhesion and poor gloss.

Penetration into the paper should be held to a minimum to keep as much coating as possible on the surface of the paper, since excessive penetration embrittles the sheet[35] and increases the comsumption of coating material. The amount of coating absorbed depends upon the initial density and porosity of the paper, since there is practically no swelling of fibers due to the solvent. The amount of internal sizing has relatively little effect on penetration. Albert[36] reports that varnishes (phenolic) penetrate papers with greater difficulty than oils of the same viscosity.

Solvents for Lacquers

The principal function of the solvent is to dissolve the resin and control the viscosity of the solution. Most resins can be dissolved in a variety of solvents so that a choice must be made, depending upon the results desired. In preparing lacquers, it is best to add the film-forming resin to the solvent and stir until dissolved. The non-film-forming resin should be dissolved separately and then added to the solution of the film-forming resin. After thorough mixing, the plasticizer and other modifiers can be added. In some cases, heat is necessary to incorporate the plasticizer with the resin.

In applying overprint spirit varnishes to printed papers, the ink in the printing may bleed into the alcohol solvent, thereby resulting in tinting around the edges of the print and between the halftone dots. This occurs when the pigment in the printing ink is not alcohol-proof. One remedy is to use printing inks made with alcohol-insoluble pigments. Another remedy is to use a lacquer or overprint varnish containing solvents which do not dissolve the pigment.

The boiling point or average molecular weight of the solvent has a pronounced effect on the viscosity of the lacquer.[37] The volatility of the solvent is an important factor in the drying of the film. Low-boiling solvents are desired from the standpoint of speeding up drying, but too rapid evaporation leads to blushing on account of condensation of water in the film. If this occurs, the trouble can be corrected by the addition of a small amount of high-boiling solvent. However, too much high-boiling solvent leads to the retention of solvent in the coating, resulting in bad odor and a loss of film strength.

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[35] V. A. Ryan, *Paper Trade J. 113*, No. 8: 87–91 (Aug. 21, 1941)

[36] G. A. Albert, *Paper Trade J. 101*, No. 11: 127–131 (Sept. 12, 1935)

[37] E. H. McArdle and E. L. Boldeschevieler, *Ind. Eng. Chem. 34*, No. 7: 882–885 (July, 1942)

Most commercial formulations are made with the aid of mixed solvents, since mixed solvents are often more effective than either solvent alone. In some cases, two non-solvents make an excellent solvent mixture when used together, e.g., chlorinated hydrocarbons and alcohol, which separately are non-solvents, but which make a good solvent mixture for cellulose esters. Many formulations contain a cosolvent, which (although not a solvent by itself) improves the solubility of the resin in the true solvent. For example, solutions of nitrocellulose (RS) in a ketone solvent often contain alcohol (cosolvent) which improves the solubility and lowers the viscosity.

Diluents are often added to solvent coatings. These cheapen the formulation, but have the disadvantage of lowering the water vapor resistance of the film. Diluents (such as naphtha and toluene) can be used in nitrocellulose lacquer when esters or ketones are used as the true solvent. They can be used in cellulose acetate lacquers when acetone or nitromethane are used as solvents, but not when alcohol is the solvent. Only a small amount of diluent can be used if the formulation contains a high percentage of natural resin.

When using mixed solvents, it is desirable that the solvents produce a constant-evaporating mixture, because otherwise the initial balance between solvents will change during drying, thus changing the properties of the film. The fact that the components of a solvent mixture have the same boiling points does not necessarily mean that the mixture will be constant-evaporating.[38] This is due to the fact that evaporation depends upon the diffusion rate of solvent in the coating film, as well as upon the difference in partial pressures between the interface and the body of the gas. The diffusion rates are dictated largely by the molecular weight of the solvent and the affinity between the solvent and the resin in the coating.[39] As a general rule, alcohols evaporate more slowly than esters, and non-solvents leave the film more rapidly than the true solvent. The rate of evaporation of the true solvent is often affected by the presence of non-solvent in the mixture.

Plasticizers

Lacquers generally contain plasticizers, which are low-melting solids or high-boiling liquids whose function it is to improve the flexibility and toughness of the film and, in some cases, to improve the heat-sealing properties. All resins do not require plasticizers, as, for example, polyethylene and cyclized rubber, which can be used alone. On the other hand, the natural resins, nitrocellulose, and many other film-forming resins must be used with plasticizers. Some resins exert a partial plasticizing effect on the other resins in the mixture and consequently can be considered as plasticizers. This is particularly true of the low molecular weight polymers.

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[38] L. Squires, W. K. Lewis and C. E. Sanders, *Ind. Eng. Chem. 27,* No. 12: 1395–1396 (Dec., 1935)

[39] W. K. Lewis and L. Squires, *Ind. Eng. Chem. 29,* No. 1: 109–114 (Jan., 1937)

Plasticizers are related to solvents, but the difference lies in the fact that plasticizers are non-volatile compounds and impart relatively permanent flexibility, whereas solvents are highly volatile and their softening effect is temporary. Plasticizers function by weakening the secondary forces (van der Waals forces) between chains of thermoplastic resins so that these chains are freer to move in relation to one another. This softening effect increases the ease with which the resin can be formed into films and imparts flexibility to the film. From the mechanical standpoint, plasticizers reduce the tensile strength and increase the elongation and elasticity of the resin film. At high concentrations, the plasticizer forms a continuous phase, but the plasticized resin, under these circumstances, is likely to be a soft gel or a liquid. The amount of plasticizer used depends upon the type of resin and the results desired, and normally varies from 10 to 25%. As a general rule, the highly polymerized resins tolerate more plasticizer than the low molecular weight resins without becoming tacky.

Two types of plasticizers are recognized, the solvent type and the non-solvent type. In general, solvent type plasticizers are undesirable because they detract from the chemical resistance and strength of the film. On the other hand, they have the advantage of high retention and consequently can be used in high proportions without danger of sweating or separation. Plasticizers must be chosen with care for such properties as freedom from odor, toxicity, volatility, compatibility with the resins used, solvent resistance, low temperature flexibility, and solubility in fats, oils, water, etc. The compatibility of the plasticizer with the resin can be determined by casting a film and examining the film for cloudiness, streakiness, crystallization, or sweating.

The permanence of the plasticizer is important, particularly in the case of paper coatings where a large surface area is exposed in relation to the mass of the coating. In general, plasticizers of high molecular weight and low vapor pressure show the highest degree of permanence. If the lacquer coating is to be baked (i.e., heated to 300 to 400° F.), consideration must be given to the effect of high temperature on the plasticizer. Many plasticizers show negligible vapor pressures at temperatures up to 150 to 200° F., but tend to evaporate very rapidly at higher temperatures, in which case there may be a substantial loss of plasticizer on baking. On the other hand, there is often an affinity between resin and plasticizer which tends to hold a low-boiling plasticizer in the coating. Loss of plasticizer when the coating is brought into contact with water is another important factor. This depends upon the water solubility of the plasticizer.

Some of the materials commonly used as plasticizers are dibutyl phthalate, tricresyl phosphate, castor oil, camphor (where odor is not important), stearates, phthalyl glycolates, dibutyl sebacate, dibutyl phthalate, butyl phthalyl butyl glycolate, and others.

Modifiers

Waxes and oils are sometimes used as modifiers in solvent coatings to increase the water and water-vapor resistance of the film and to lubricate the coated surface. In certain coatings the wax is believed to migrate to the surface, forming a thin but highly water-resistant surface film. If too much wax is used, a condition known as wax blush occurs, due to the appearance of an excess of wax on the surface. Treatment of the surface of the coated paper with a 5 to 10% solution of wax in a suitable solvent (e.g., naphtha) is said to accomplish the same purpose as adding wax to the coating formulation.[40]

Paraffin, paraffin oil, stearin, and soap may be added to resinous coatings to increase the slip. Dyes may be added for tinting. Pigments may be added for color and opacity. In general, the hiding power of the pigmented coatings depends upon the pigment volume concentration in the coating mixture. In the case of baking varnishes containing titanium pigment and urea-alkyd resin binder, Armstrong and Madson[41] obtained maximum hiding power at a pigment concentration of 25% by volume.

Use of Non-Film-Forming Resins

The function of non-film-forming resins in lacquers is to impart luster to the film, to increase the resistance to oil, grease, and water, to increase the solids content, and to increase the wax tolerance. Certain resins increase the hardness of the film, whereas others have a plasticizing effect. Too much non-film-forming resin cannot be used, since it tends to lower the block resistance and flexibility of the film.

Among the natural resins used are manila, shellac, zein, dammar, pontianak, rosin, and rosin derivatives. Shellac is widely used for making food wrappers, shelf papers, and holiday wrapping papers. Shellac coatings have high grease and oil resistance, but low water resistance. Zein is sometimes used as a substitute for shellac.

Rosin derivatives are becoming increasingly important. The rosin-derived alkyd resins (Neolyn resins) can be used in nitrocellulose lacquers or vinyl resin lacquers to increase the adhesion and gloss of the coatings A suitable formula for the use of this rosin derivative in lacquer is:[42]

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[40] F. K. Shankweiler, *Pulp Paper Mag. Canada 37,* No. 8: 445–450 (July, 1936)

[41] W. G. Armstrong and W. H. Madson, *Ing. Eng. Chem. 39,* No. 8: 944–947 (Aug., 1947)

Non-volatiles

RS ½ sec. nitrocellulose (dry basis)	21 parts
Rosin-derived alkyd resin (Neolyn 24)	7 parts
Dibutylphthalate	7 parts

Solvents

Toluene	35.7 parts
Butyl acetate	13.0 parts
Ethyl acetate	6.5 parts
Ethanol	6.5 parts
Butanol	3.3 parts

Figure XXII-1[42] shows the effect of rosin-derived alkyd resins (Neolyn resins) on nitrocellulose lacquers. Other rosin derivatives, such as the methyl ester of rosin (Abalyn resin) and the hydrogenated methyl ester of rosin (Hercolyn resins) can be used in nitrocellulose lacquers to improve the gloss. When used in ethylcellulose films, these resins decrease the water sensitivity. These derivatives are classed as resin plasticizers.

In recent years the trend has been away from natural resins toward the use of synthetic resins. Some of the most important synthetic non-film-forming resins used are the solvent-soluble grades of urea-formaldehyde, melamine-formaldehyde, phenol-formaldehyde, coumarone-indene, terpene, modified and unmodified alkyds, and the aryl sulfonamide-formaldehyde resins.

The phenol-formaldehyde resins are used in solvent coatings where color is not important, but where good chemical, heat, and electrical resistance are necessary. The modified phenolic resins are most widely used. The solvent-soluble grades of urea- and melamine-formaldehyde resins are used in solvent coatings where color is of importance. Melamine resins have the greater stability, but are more expensive.

The alkyd resins, particularly the modified grades (see chapter on Resins), are used in solvent coatings. These resins have good electrical properties and a high degree of grease resistance, but their water resistance is rather poor. One use for alkyd resins is in baking varnishes for coated pie plates and other dishes used for baking food products. The resin is applied in solvent form and then is cured at 280 to 350° F. to produce a hard, durable, heat-resistant coating on the surface of the board. The paper used for this product should be as nearly neutral as possible in order to obtain the least embrittlement on heating.[43] Usually sulfite or sulfate papers are used.

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[42] "The Neolyns, A New Series of Resins," Synthetics Dept., Hercules Powder Co., Wilmington, Delaware

The aryl sulfonamide-formaldehyde (Santolite) resins can be used in nitrocellulose lacquers in a ratio of 1 part resin to 2 parts nitrocellulose to increase the moisture resistance and increase the hardness of the film. In cellulose acetate lacquers, this resin increases the retention of the plasticizer and imparts oil and gasoline resistance to the film. In ethylcellulose lacquers, the resin increases the flexibility and toughness of the film. In vinyl copolymer lacquers, the resin improves adhesion, gloss and light stability without materially changing the hardness and flexibility of the film. Some practical formulas are given below.[44]

Nitrocellulose lacquer for brushing

RS (½ sec.) nitrocellulose	1 part
Aryl sulfonamide-formaldehyde resin (Santolite MHP)	2 parts
Butyl benzyl phthalate (Santicizer 160)	0.5 part
Butyl acetate	3.6 parts
Butanol	1.2 parts
Xylene	7.2 parts

Cellulose acetate lacquer

Cellulose acetate (Hercules LL-1)	6 parts
Aryl sulfonamide-formaldehyde (Santolite MHP)	6 parts
Methyl phthalyl ethyl glycolate (Santicizer M-17)	3 parts
Acetone	41 parts
Ethanol	5 parts
l-nitropropane	17 parts
Methyl cellosolve acetate	16 parts
Toluene	6 parts

Polyvinyl resin lacquer

Polyvinyl resin (Vinylite VYHH)	70 parts
Aryl sulfonamide-formaldehyde (Santolite MHP)	10 parts
Dioctyl phthalate	20 parts

The final solids are 42% by weight in a solvent composed of equal parts of methyl ethyl ketone, cyclohexanone, and toluene.

The coumarone-indene and phenol-modified coumarone-indene resins are used in solvent coatings where low cost and a high degree of chemical resistance are required, and where poor odor and color are not objectionable. A recommended formula is:[45]

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[43] V. A. Ryan, *Paper Trade J. 113*, No. 8: 87–91 (Aug 21, 1941)

[44] Technical Bulletin O-D-112, "Santolite MHP," Development Dept., Organic Chemicals Division, Monsanto Chemical Co., St.Louis, Missouri

[45] Bulletin, "Neville Resins and Plasticizers," The Neville Co., Neville Island, Pittsburgh, Pennsylvania

Nitrocellulose (½ sec.)	136	parts
Phenol-modified coumarone-indene resin (Nevillac Pale Hard)	42	parts
Dibutyl phthalate	48	parts
n-Butyl acetate	200	parts
n-Butanol	52	parts
Toluol	324	parts
Ethyl acetate	67	parts

Use of Film-Forming Resins

Film-forming resins are used in lacquers to increase the toughness and flexibility of the film, to improve the resistance of the film to moisture and cold check, and to reduce the tendency toward blocking. A few of the common film-forming resins used in lacquers are nitrocellulose, ethylcellulose, cellulose acetate, cellulose acetate-butyrate, polyethylene, vinyl chloride, vinyl acetate, vinyl chloride-acetate, polyvinylidene copolymers, polystyrene and methacrylate resins. Only the film-forming resins which dissolve in the common solvents (alcohols, esters, aromatic or aliphatic hydrocarbons, ketones, etc.) and which produce continuous and transparent films are practical for solvent coatings.

The viscosity of the film-forming resin is an indication of film strength and, in general, the higher the viscosity, the stronger and more flexible the film (see Fig. XXIII-3). On the other hand, high-viscosity resins require a high proportion of solvent which increases the cost and the difficulty of application. Thus, a compromise must often be made.

In working out a lacquer formula, the proper film-forming resin is selected on the basis of the properties desired. Plasticizer is then added to determine the maximum amount of plasticizer which the resin will tolerate without forming too soft a film. Then, using about one-half this amount of plasticizer, sufficient non-film-forming resin is added to obtain the desired film properties. The amount of added resin should be less than that which causes blocking or tackiness of the film. If more complete information is desired, ternary diagrams can be constructed (see Fig. XXII-1).

In the following sections, the general use of film-forming resins in solvent coatings is discussed. These are by no means the only film-forming resins which can be used, but instead represent a few of the more important resins selected to illustrate the various methods of formulation and application.

Use of Nitrocellulose. Nitrocellulose is widely used in lacquer coatings because of its relative cheapness, its compatibility with a wide range of resins, its solubility in a wide range of solvents, and its good film-forming properties. The solvents used with the RS type of nitrocellulose are ethyl acetate, butyl acetate, acetone, and methyl ethyl ketone. Mixed solvents are generally used commercially (for example, a mixture of ester, alcohol, and toluene). Alcohols act as cosolvents and lower the viscosity, whereas hydrocarbons act as thinners and cheapen the mixture.

The ¼-second grade of nitrocellulose is used where lacquers of maximum solids content are desired. The 5–6-second grade is preferred if maximum folding qualities are required in the finished coating. The intermediate ½-second grade is often used, and in some cases, mixtures are used. Nitrocellulose lacquers do not lend themselves well to brushing, but other forms of application can be used.

The weight of nitrocellulose applied varies from about 2 to 5 lb. per ream (24 × 36—500) for glassine paper to about 5 to 10 lb. per ream for label paper and carton board.[46] The water vapor resistance obtained with glassine coated with different formulations of nitrocellulose lacquer are shown in Table II in comparison with waxed papers.[46] The advantage of incorporating wax in the formula is apparent.

TABLE II

WATER VAPOR TRANSMISSION OF GLASSINE COATED WITH NITROCELLULOSE LACQUERS IN COMPARISON WITH OTHER MATERIALS

Type of material	Water vapor transmission, g./100 sq.in./24 hr.
Moistureproof regenerated cellulose	0.1–0.5
Glassine	33
Glassine coated with ordinary nitrocellulose lacquer	14
Glassine coated with high resin nitrocellulose lacquer	3
Glassine coated with nitrocellulose lacquer containing wax	0.2
Glassine coated with wax (full waxed)	0.2–0.6
Sulfite (dry waxed)	5.8
Sulfite (full waxed)	0.2–0.8

The alkyd resins (both drying and non-drying oil types), the polyester or plasticizing type of alkyd resin, and rosin esters are examples of some of the non-film-forming resins which are used in nitrocellulose lacquers. These resins tend to reduce the hardness of the coating, improve the heat seal and enhance the gloss and depth of finish. With certain of the plasticizing type resins, no other plasticizer is needed. A ternary diagram showing the effect of rosin-derived alkyd resin (Neolyn 41 resin) in nitrocellulose (RS-½ sec.) lacquer is shown in Figure XXII-1[47] The areas in the figure may be classified as follows:

A	flexible, non-blocking, non-tacky
B	brittle, non-blocking, non-tacky
C	flexible, blocking, non-tacky
D	brittle, blocking, non-tacky
E	flexible, blocking, tacky
F	brittle, blocking, tacky

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[46] F. K. Shankweiler, *Pulp Paper Mag. Canada 37*, No. 8: 445–450 (July, 1936)

In this diagram, the most useful area is in the lower left-hand corner of area *A* (shaded area), since this represents the area of composition in which the greatest amount of resin can be incorporated without losing block resistance and flexibility. The various formulas were tested by applying the lacquer to a supercalendered sulfite paper (22 lb. 24 × 36—500), using a knife coater. The coating weight was 8 lb. per ream, and the coated paper was dried for fifteen to twenty minutes at room temperature, after which it was force-dried for two minutes at 120° C. A small amount of ethylcellulose may be added to nitrocellulose lacquers to reduce cold check.

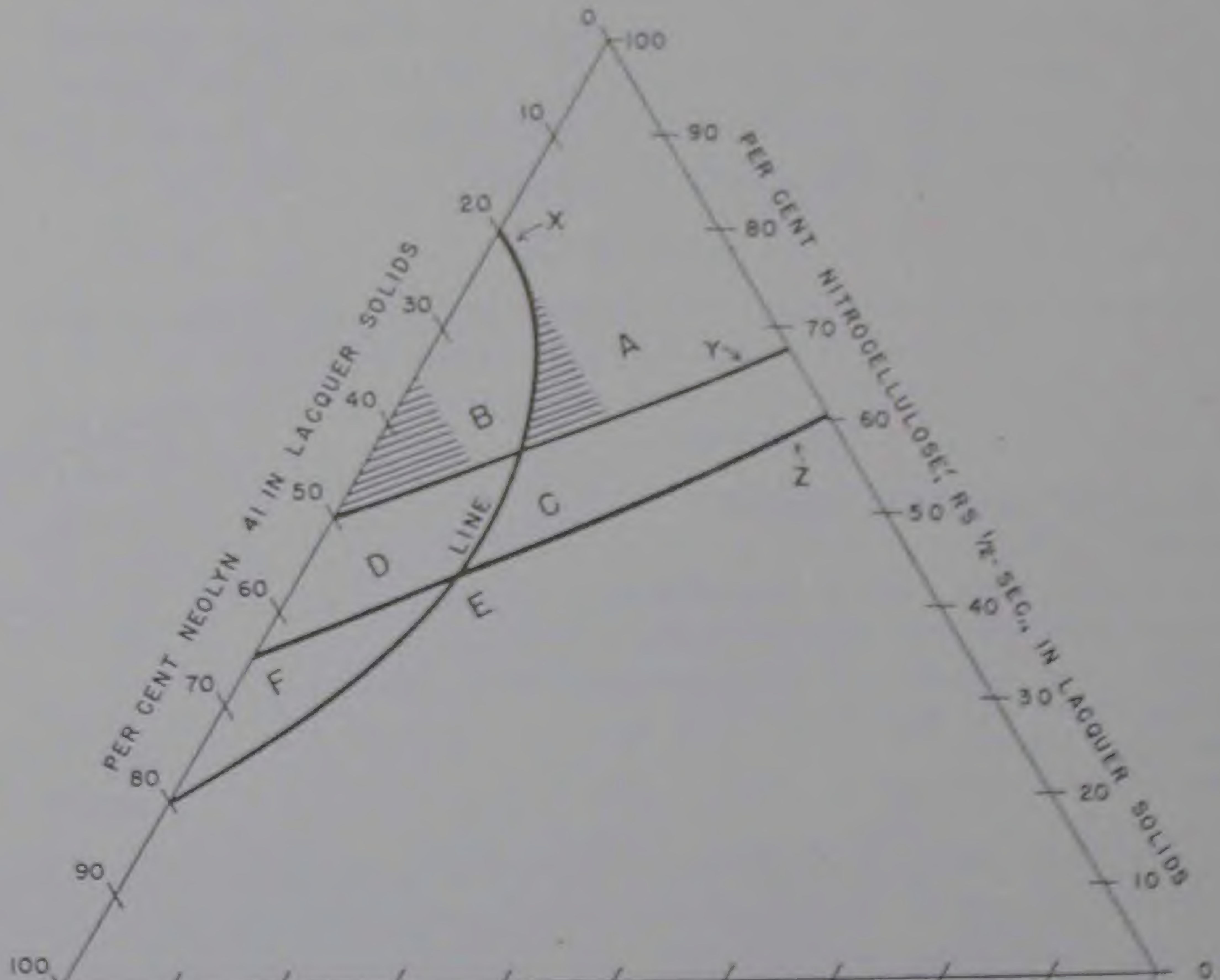

Fig. XXII-1. Effect of rosin derived alkyd resin on properties of nitrocellulose films.[47] X demarks flexible (to right) and brittle (to left). Y demarks blocking (below) and non-blocking (above). Z demarks tacky (below) and non-tacky (above).

Use of Ethylcellulose. Ethylcellulose is used in lacquers where a high degree of film flexibility and good heat-seal properties are desired. Ethylcellulose is soluble in practically all types of lacquer solvents except petroleum thinners. It is soluble in straight alcohol and can be applied from a mixture of ethanol and butanol (70–30). However, it is generally used in solvent mixtures containing 60 to 80% aromatic hydrocarbon, and 20 to 40% alcohol. No more than 40% alcohol should be used, since the greatest strength and flexibility are obtained when the aromatic solvent is the last to evaporate from the film.[48] The addition of alcohol to ethylcellulose in toluene results in a reduction in viscosity, the greatest reduction in viscosity being obtained with the low molecular weight alcohols. The minimum viscosity is obtained when alcohol constitutes about 20 to 30% of the total solvent. The following represents a suitable solvent mixture for ethylcellulose in the ethoxy range of 48.5 to 49.5%.[49]

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[47] Courtesy "Hercules Resins for Paper Lacquer," Synthetics Dept., Hercules Powder Co., Wilmington, Delaware

Toluene	40 parts
Xylene	30 parts
Ethyl alcohol	15 parts
n-Butyl or amyl alcohol	15 parts

High-solvent naphtha may be substituted for the toluene. In the medium ethoxy range (45.0–46.5%), slightly more alcohol should be used. Resins are added to improve the gloss, adhesion, solvent resistance, and rubbing properties of the film, and normally, about 15 to 30% plasticizer is added (see Ch. XXIII).

Use of Polyvinyl Acetate and Polyvinyl Chloride. Polyvinyl acetate is used in lacquers where good adhesion, good heat-seal properties, and good flexibility are desired. It is used in protective overlacquers for printed paper labels, posters, and decorative papers, and is also used as a heat-seal adhesive. Polyvinyl acetate is soluble in most solvents, including alcohols, ketones, and aromatic hydrocarbons (see Ch. XXIII). The lacquers can be applied by dipping, roll-coating, knife-coating, or brushing. Spraying is not practical with vinyl resins, except in the low-viscosity grades, because of the tendency to string or cobweb. The film is usually dried and then baked for a few minutes at 225 to 250° F. to release the solvent. Forced convention ovens or infrared lamps can be used. A small amount of nitrocellulose (10 to 25%) may be incorporated in the lacquer to raise the softening point.

Polyvinyl chloride coatings have excellent oil and solvent resistance and are used for paper oil containers and paper gaskets. Polyvinyl chloride is, however, relatively insoluble in most solvents, and even when dissolved, must be used at low solids. This fact has limited its use in solvent coatings.

Use of Polyvinyl Chloride-Acetate Copolymers. Polyvinyl chloride-acetate copolymers produce lacquers with low viscosity and rapid evaporating properties. They are used for coating decorative papers, heat-sealing papers, paper drum linings, grease-proof papers, and milk bottle caps. The films are tough and have a high degree of water, grease, solvent

[48] T. A. Kauppi and S. L. Bass, *Ind. Eng. Chem. 30:* 74 (1938)

[49] Technical Bulletin, "Dow Coating Materials, Ethocel," The Dow Chemical Co., Midland, Michigan (1947)

and chemical resistance, and are quite flexible at low temperatures. The films are also quite resistant to water vapor. Because the films are resistant to alkali, the resin can be used on alkaline wallboards and soap wrappers. Supercalendered sulfite, glassine, greaseproof, and parchment are some of the papers used for coating.

The copolymer containing 87% vinyl chloride and 13% vinyl acetate is one of the most suitable grades for paper coating lacquers. This resin is soluble in a wide variety of solvents, but mixtures of ketones and aromatic hydrocarbons are the most practical. Methyl ethyl ketone is widely used, although for brushing, slow-evaporating solvents (methyl *n*-amyl ketone, mesityl oxide, or cyclohexanone) may be required. The aromatic hydrocarbons can be slower evaporating than the ketone because of the solubility of the resin in hydrocarbons at elevated temperatures.[50] Low-viscosity grades require a high percentage of ketone. The ratio of ketone required also depends upon the solids content of the lacquer, and for the highest practical solids (about 20%), a ratio of 50–50 ketone to aromatic hydrocarbons is required. Figure XXII-2[51] shows the equilibrium viscosities of the medium viscosity polymer in different mixtures of methyl ethyl ketone and toluene at various solids content. Above about 20% solids, the lacquer becomes quite thixotropic. Figure XXII-3[51] is a phase diagram showing the type of flow behavior obtained at different concentrations of resin and different ratios of solvent (methyl ethyl ketone) to diluent (toluene) at 20° C.

In preparing a lacquer from this resin, the resin is added slowly to the solvent under vigorous agitation. If considerable diluent is to be used, the resin should first be mixed with the diluent and then the solvent added. Heat is generated during mixing, but additional heat may be desirable to obtain complete solution. In order to avoid discoloration in the presence of iron, about 0.1 to 0.3% of propylene oxide based on the weight of the resin may be added.

Another useful copolymer is that composed of 62% vinyl chloride and 38% vinyl acetate. This resin is compatible with nitrocellulose and other vinyl resins in the presence of a small amount of plasticizer. If used with nitrocellulose, the alcohol content of the lacquer should be kept to a minimum.

In order to obtain maximum water vapor resistance with polyvinyl chloride-acetate copolymers, a small amount (1 to 5%) of paraffin may be added. The wax is not compatible with the resin, but can be dissolved in hot toluene and added to the resin solution where it is held in fine sus-

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[50] C. W. Patton, *Official Digest*, New York Paint and Varnish Production (May, 1948)

[51] Courtesy "Vinylite Resins for Surface Coatings," Bakelite Corporation, Carbide and Carbon Chemicals Corp., New York, N. Y. (1942)

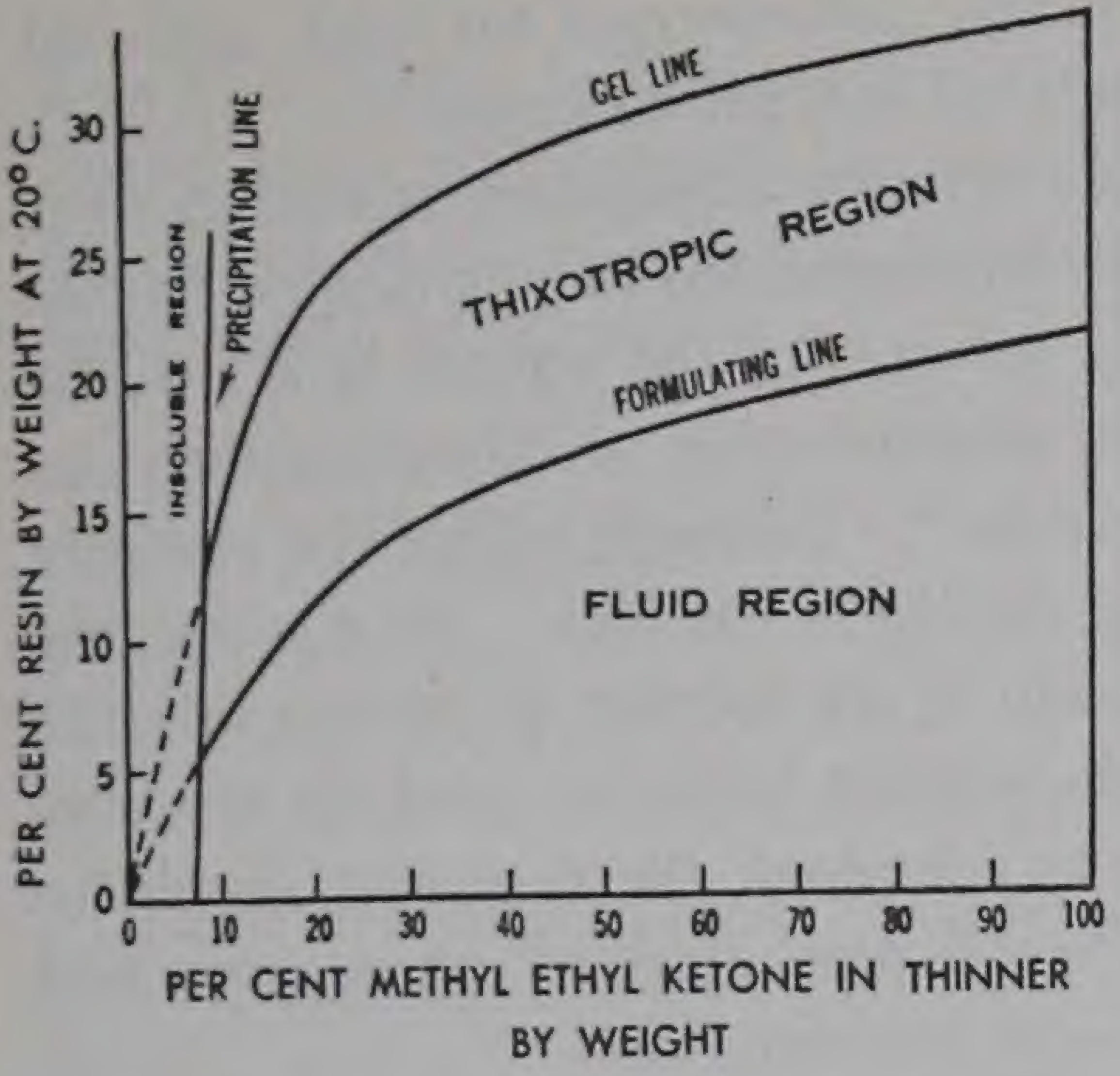

Fig. XXII-3. Flow behavior of polyvinyl copolymer in mixtures of methyl ethyl ketone and thinner (toluene). Courtesy Bakelite Corporation.

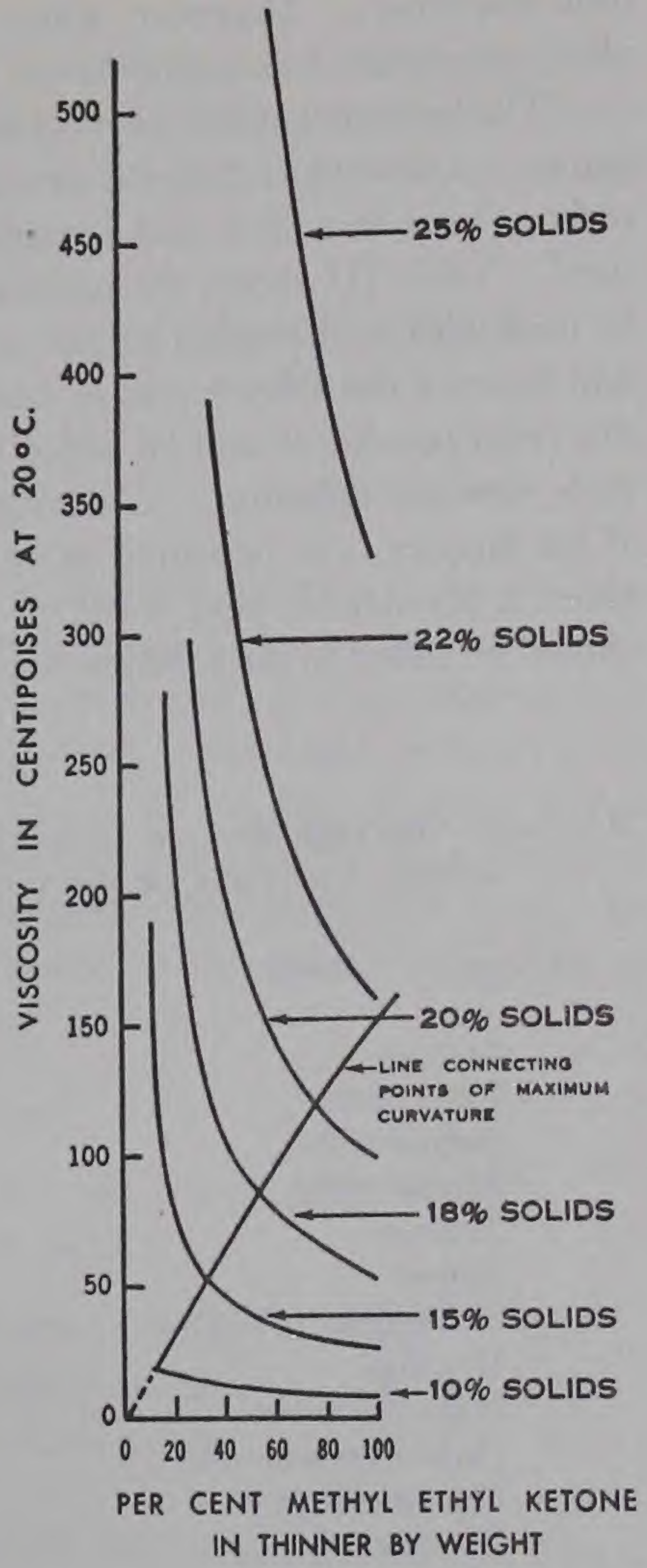

Fig. XXII-2. Viscosity of polyvinyl copolymer resin in mixtures of methyl ethyl ketone and thinner (toluene). Courtesy Bakelite Corporation.

pension. Resin solutions containing wax work best on non-porous papers which do not absorb too much of the wax.

For best results with polyvinyl copolymer lacquers, it may be necessary to apply several different coats. The first coat serves for anchorage of the coating to the paper, the second coat serves to build up the film, and the final coat acts as a sealing coat.[52] Drying of the coating must be carried out slowly at temperatures no greater than 160° F.

Use of Polyvinylidene Chloride Copolymers. Lacquers made from polyvinylidene chloride copolymers form very dense and flexible films which have a high degree of resistance to water, water vapor, and grease, and have good heat-sealing properties. The resins have been used for coating paper milk containers. However, when suitably polymerized for high acid and alkali resistance, this resin[52] is too inert for solvent coatings.

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[52] H. W. Foelsch, *Paper Trade J. 129,* No. 25: 501–502 (Dec. 22, 1949)

The best solvent for polyvinylidene chloride copolymers is methyl ethyl ketone. Diluents such as the aromatic hydrocarbons or chlorinated hydrocarbons may be added, and secondary solvents of the acetate type may be used. Table III shows the maximum concentration of diluents which can be used with methyl ethyl ketone solutions.[53] Diluents reduce the viscosity and improve the solvent release during drying of the film. To dissolve, the dry resin powder should be added slowly to the solvent or solvent mixture with vigorous agitation. Warming the solvent helps to speed up solution. If the lacquer is to be stored in an iron container, the container should be given a phosphoric acid wash, or a small percentage of phosphoric acid should be added to the solution to prevent discoloration.

TABLE III

MAXIMUM CONCENTRATION OF DILUENT THAT CAN BE ADDED TO METHYL ETHYL KETONE SOLUTIONS OF POLYVINYLIDENE-ACRYLONITRILE COPOLYMER

Diluent	Percentage by volume of methyl ethyl ketone that can be replaced without gelation at 25° C.
Acetone	75%
Ethyl acetate	60%
Butyl acetate	50%
Nitromethane	25%
Toluene	30%
Xylene	20%
Skellysolve (60–70° C.)	10%
Methanol	25%
Isopropyl alcohol	15%
Carbon tetrachloride	10%
Chlorobenzene	30%
Dioxane	90%

The lacquer may be applied by brush, dip, knife, or roller application, but cannot be sprayed except at low concentrations because of the rapid solvent release in the early stages of drying. All solvent must be removed during drying to obtain the maximum resistance to water vapor. For drying a coating composed of about 14 lb. of resin per 3,000 sq. ft. (coating 0.6 mil in thickness), the paper should be passed through an oven which gradually increases in temperature from 95 to 300° F. in approximately two minutes; then the coating should be subjected to a flash bake at 500° F. for approximately ten seconds, and finally passed over a cooling roll.[53] If the coating is 1 mil or over in thickness, a slower drying schedule must be followed (or higher boiling solvents used) in order to prevent blistering. Infrared lamps can be used for removing the last traces of solvent. Polyvinylidene chloride copolymer coatings have water-vapor resistance approximately as follows :[53]

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[53] Technical Bulletin, "Dow Coating Materials, Saran F-120," The Dow Chemical Co., Midland, Michigan (1946)

Thickness of coating, mil	M.V.T. g./100 sq.in./24 hr. at 100° F. and 95 R.H. differential
0.6	0.25
1.0	0.15

Use of Polyethylene. Polyethylene produces films having good flexibility at low temperatures, and hence is well suited for frozen food wrappers. Heat sealing can be readily accomplished, particularly if the surface is prewetted with mineral oil. The films have high water vapor resistance but low resistance to other gases. A comparison of the gas permeabilities of polyethylene and vinyl resin films are shown in Table IV.[54] Film thickness was 0.002 in. in both cases and measurements were made with a vacuum on one side and gas at atmospheric pressure on the other. Properties of polyethylene are discussed further in Ch. XXIII.

TABLE IV

GAS PERMEABILITY OF POLYETHYLENE AND VINYL RESIN FILMS
(cc./100 sq. in./24 hr.)

Resin	Oxygen	Nitrogen	Carbon dioxide	Moisture vapor
Polyethylene	320	70	1500	0.5
Vinyl, containing 20% plasticizer	32	9	82	2.0

The grade of polyethylene most widely used in lacquers is the resin of medium molecular weight, i.e., about 20,000.[55] The resin is dissolved and applied hot. If the temperature is lowered, the resin precipitates from solution but solution can again be obtained by reheating. Figure XXII-4[54] shows the solubility of commercial polyethylene resin in several different solvents at different temperatures. At 90° C., a 35% solution can be obtained in toluene. A phase diagram for polyethylene-xylene system is shown in Figure XXII-5.[54]

Polyethylene lacquer can be applied by reverse roll coaters or by spreader knives. Hot knives or heated applicator rolls are desirable to maintain the temperature over 90° C. Immediately after application, before cooling occurs, the coated paper should enter an oven at high temperature. All solvents must be removed before the coating cools to the point of precipitation in order to prevent poor film formation. Maximum film strength is obtained by baking at temperatures of about 150° C. A coating about 1 mil in thickness is obtained by applying 15 lb. of coating per 3,000-sq. ft. ream.[56]

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[54] Technical Bulletin No. 7, "Polyethylene Resins," Bakelite Corp., Carbide and Carbon Corp., New York, N. Y.

[55] Sold as DYNH by Bakelite Corporation

Use of Rubber and Rubber Derivatives. Natural rubber is not used to any extent in solvent coatings because of its poor solubility characteristics. However, some of the rubber derivatives and synthetic rubbers are used in solvent coatings.

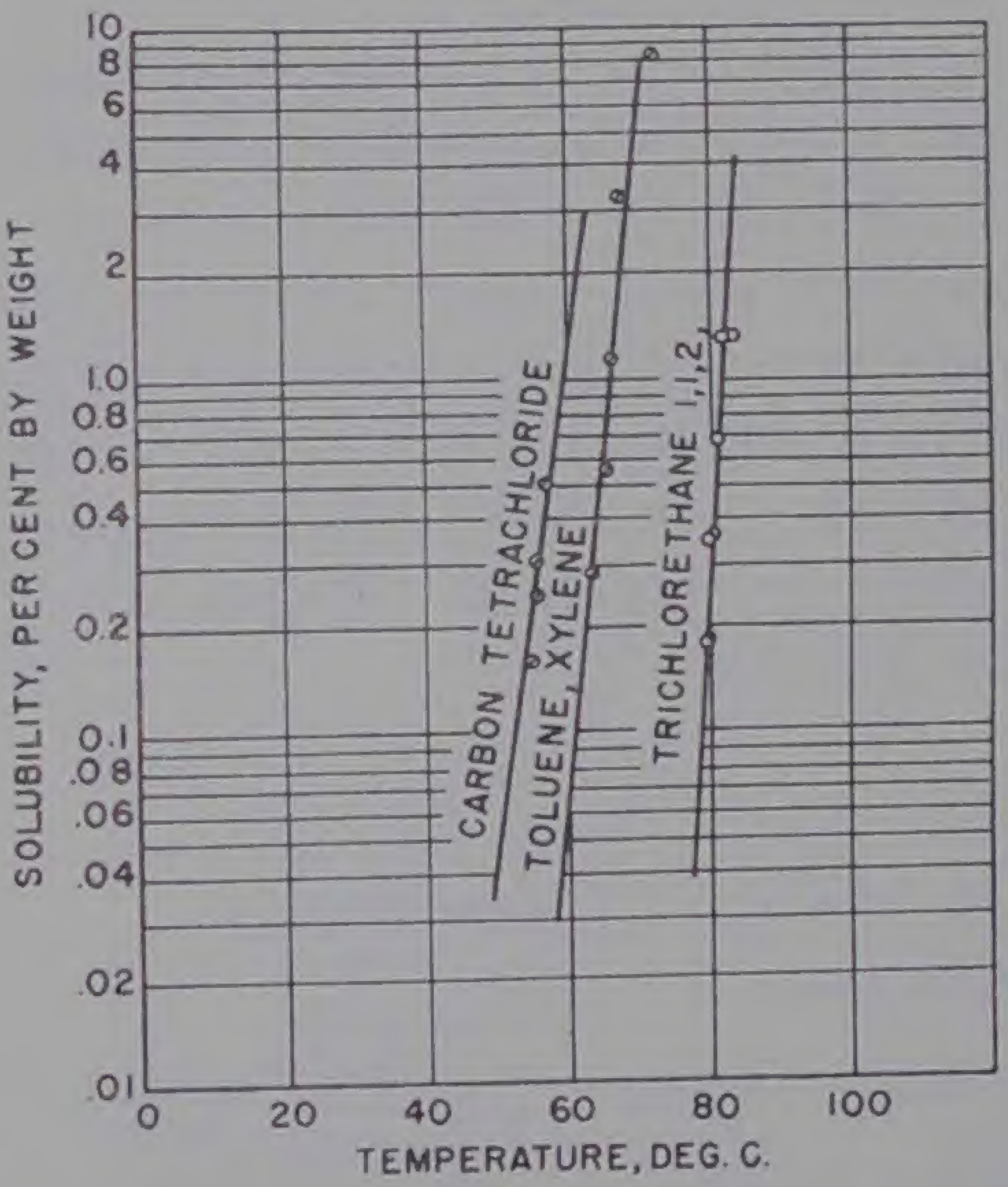

Fig. XXII-4. Solubility of polyethylene resin in different solvents at different temperatures.

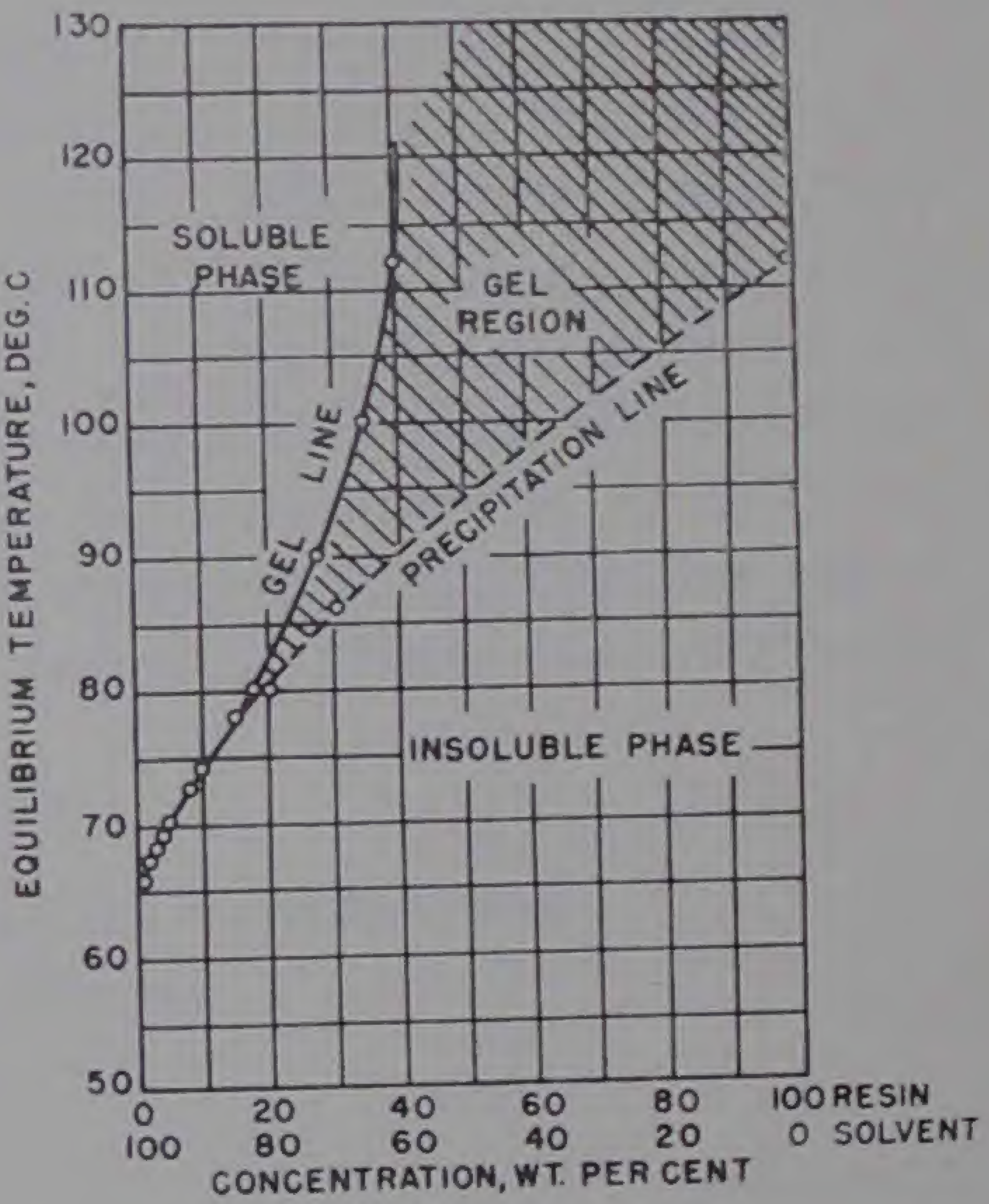

Fig. XXII-5. Phase diagram for polyethylene resin-xylene system. Figs. 4 and 5 courtesy Bakelite Corporation.

Cyclized rubber produces flexible, heat-sealable, and highly water-vapor resistant coatings when applied in very thin films from either aromatic or aliphatic hydrocarbon solvents. Table V shows the drying characteristics of cyclized rubber films deposited from different solvents.[57] The results also show comparative viscosities in the different solvents. The effect of film thickness on water vapor resistance is shown in Figure XXII-6[57] for both coated glassine and coated label stock.

Chlorinated rubber is readily soluble in both aromatic and aliphatic hydrocarbons and can be applied to paper from these solvents. Chlorinated rubber produces films with a high degree of chemical resistance, but wax must be added if high water vapor resistance is desired. Rubber hydrochloride, on the other hand, is not widely used because of its poor solubility.

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[56] J. K. Honish, *Paper Trade J. 128,* No. 15: 125–127 (Apr. 14, 1949)

[57] H. R. Thies, *Paper Trade J. 108,* No. 8: 79–84 (Feb. 23, 1939)

However, a mixture of rubber hydrochloride with vinylidene chloride copolymer dispersed in benzene has been suggested.[58]

Some of the newer synthetic rubbers are soluble in a wide range of solvents and produce coatings having interesting properties. Latham[59] describes a mixture of polyisobutylene with polyethylene. A relatively new butadiene-styrene product, called S-7 resin, has excellent properties for lacquer type coatings (see Ch. XXIII). This material may be used in unmodified or modified form, the latter types being most useful. A typical formula is (see also p. 1349):[60]

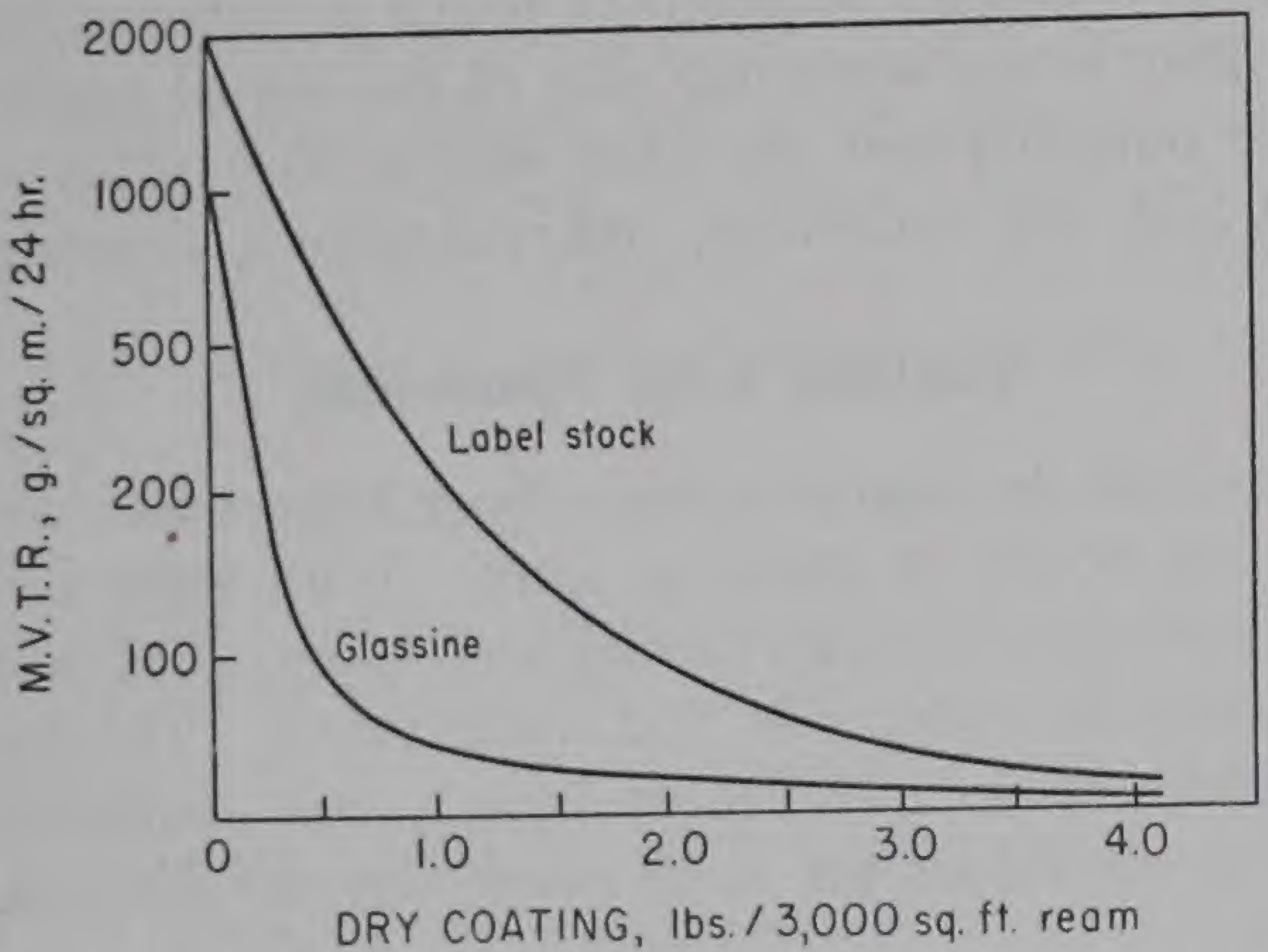

Fig. XXII-6. Effect of film weight on the water-vapor resistance of cyclized rubber coatings.

TABLE V

COMPARATIVE VISCOSITIES AND DRYING TIMES OF CYCLIZED RUBBER IN VARIOUS SOLVENTS

Films 0.001 in. thick

Solvent	Viscosity, Ford cup 74° F.—#4 orifice	Drying time, 79° F.—25% R.H., min.
Benzene	1.70	1.5
Skellysolve D	1.13	3.25
Skellysolve C	1.21	3.00
Xylene	1.68	13.50
Varnish makers' naphtha	2.0	53.0
Turpentine	6.0	28.5

S-7 resin	100
Modifying wax	15
Modifying resin	10
Toluene	500

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[58] F. H. Manchester, U. S. 2,386,700 (Oct. 9, 1945)

[59] G. H. Latham, U. S. 2,369,471 (Feb. 13, 1945)

[60] Bulletin No. 701, "Pliolite," The Goodyear Tire and Rubber Co., Akron, Ohio

Wax increases the resistance to water vapor and raises the blocking point of the film, but no more than 15% wax should be used, since this lowers the heat seal. Microcrystalline waxes (melting points of about 170° F.) are recommended. Glassine paper coated with 1 lb. per 1,000 sq. ft. of the above formulation transmits between 0.2 to 0.3 g. water vapor per 100 sq. in. per twenty-four hours when one side of the coated paper is subjected to 20% relative humidity and the other side to 95% relative humidity at 100° F. Heat seal, slip, anchorage, and resistance to creasing are good.

Coating with Emulsions

Recent advances in emulsion technology have made available many good film-forming resins in emulsion form. With these new emulsions, it is possible to produce coatings having high gloss, good scuff resistance, and good resistance to water, oils, and water vapor. The emulsions used in the paper industry include rubber latices, wax emulsions, and resin emulsions. Wax emulsions are used mostly for the internal and surface sizing of paper.

Rubber (natural and synthetic) latices produce results quite different from that of the synthetic resin latices. Rubber latices deposit films which are definitely rubbery in nature; that is, the film is resilient and can be stretched many times its original length, and when released, returns to approximately its original dimensions. Because of these characteristics, rubber latices are better suited for impregnation and saturation than they are for coating. On the other hand, the synthetic resin latices yield films which are much harder, less resilient, show less elongation, and do not recover so well from stretching. In fact, some resin latices (e.g., vinyl resins) deposit films which are powdery in nature unless the resin is plasticized. However, when properly compounded, synthetic resin latices produce hard, flexible, tough films which are resistant to grease, chemicals, moisture, and abrasion. Consequently, synthetic resin emulsions are often used for coating.

All the rubbers, with the exception of the isobutylene type, are available commercially in the prepared latex form. These are made by emulsion polymerization, whereby the proper type and amount of monomers are charged to a reactor together with water, emulsifier, catalyst, and modifier and the reaction carried out at the proper temperature and for the proper time to obtain a latex of the desired physical and chemical properties. Stabilizing agents, antioxidants, vulcanizing agents, and plasticizers can be added to the resulting latex. Since isobutylene rubbers are not made by emulsion polymerization, they are not available in latex form, although aqueous dispersions of the rubber have been made.

Emulsions have the advantage of lower cost, less fire hazard, and greater ease of application, compared with solvent coatings. High-viscosity materials can be applied in emulsion form at high solids content. On the other hand, low-solids emulsions can be used when light-weight coatings are desired by diluting the emulsion with thickening agents. Emulsions can be sprayed without stringing, which is an advantage over the solution type of application. The early emulsions had the disadvantage of lack of stability against freezing and electrolytes, but recently highly stable types have been produced. The drying time of emulsions is slower than that of solvent coatings, and emulsions also tend to cause curling and warping of the paper.

Formulation of Aqueous Emulsions

Emulsions can be purchased in prepared form, or they can be made at the converting plant by emulsifying solid resins. The properties of the emulsion depend upon the type of resin, amount of emulsifying agent used, and amount of agitation available. In preparing or diluting emulsions, clean water of low dissolved salt content should be used. There are two types of aqueous emulsions, those in which the resin is dispersed directly in an aqueous medium and those in which the resin is dissolved in an organic solvent before dispersing in an aqueous medium. Some of the materials used in formulating emulsions are discussed below. These materials are usually present in the emulsion as purchased, although in some cases they may have to be added by the user.

When making an emulsion from a solid resin, the type of solvent used for dissolving the resin prior to emulsification is very important. If the emulsion is to be used on porous surfaces, low-boiling solvents should be used. On the other hand, high-boiling solvents should be used on relatively non-porous surfaces in order to avoid blushing on drying. The ratio of lacquer phase to water phase should be as high as practical. There should be a high ratio of lacquer to resin, particularly if low temperatures are used in drying.

The most important factors in the stability of the emulsion are the type and the amount of emulsifying agent used. As a rule, the emulsifying agent is carried in the water phase, although in some cases it may be carried in the lacquer phase. Normally, 2% or less is used on the weight of the water present since emulsifying agents generally reduce the water resistance of the film. However, certain emulsifying agents (e.g., ammonium oleate) can be used which decompose during drying and do not reduce the water resistance. If ammonium oleate is used as the emulsifying agent, oleic acid may be added to the lacquer phase and ammonium hydroxide added to the water phase. During drying, ammonia is removed and the small amount of oleic acid remaining blends with the resin. One disadvantage is that ammonia causes yellowing of certain solvents. Emulsifying agents tend to be absorbed by the paper, which reduces their effect on the water sensitivity of the film.

Plasticizers are added to emulsions to increase the elongation and flexibility of the film. This, in turn, increases the tear resistance of the film, but lowers the tensile strength. As a rule, plasticizers reduce the chemical resistance. Anti-oxidants are added to prevent deterioration of the physical and optical properties of the film upon aging. Stabilizers are frequently necessary to stabilize the emulsion against coagulation. Thickening agents (methylcellulose, carboxymethylcellulose, casein, etc.) are sometimes added to control the viscosity of the emulsion and to aid in keeping the coating on the surface of the paper.[61] The water vapor resistance of the coating can generally be greatly improved by incorporating a fairly high percentage of wax emulsion in the formula; for best results, the coating must be heated above the melting point of the wax during drying. Other materials which may be added include wetting agents and vulcanizing agents.

The following is a general description by which a rosin-derived alkyd resin (Neolyn resin) can be emulsified.[62] This procedure is, of course, not suitable for all resins, but it illustrates a general method of emulsion preparation.

(*1*) The resin is dissolved in the solvent (in this case, xylene).
(*2*) Oleic acid is added to the resin solution.
(*3*) Potassium hydroxide dissolved in water is added dropwise with rapid stirring.
(*4*) A solution of stabilizing agent is added (in this case, ammonium caseinate).
(*5*) Water is added slowly with agitation until the system reverses itself to the desired oil-in-water type.
(*6*) Diluent water is then added.

The composition of the final resin emulsion is:

Resin	40%
Solvent	10%
Oleic acid	0.25%
Primary water	23.5%
Potassium hydroxide	0.25%
Ammonium caseinate	1.5%
Secondary water	24.5%
Casein preservative	0.015%

Emulsions can be prepared from the glycol esters of hydrogenated rosin (Staybelite resins). The resin is dissolved in a suitable organic solvent and then is dispersed with the aid of potassium hydroxide, oleic acid, and sulfated castor oil to produce emulsions ranging from 37 to 45% solids.

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[61] L. H. Silvernail, *Tappi 32*, No. 6: 246–250 (June, 1949)

[62] "The Neolyns, A New Series of Resins," Synthetics Dept. of Hercules Powder Co., Wilmington, Delaware

Two methods may be used. In the first method, a minimum of emulsifier is added and a colloid mill used for dispersing the resin. In the second method, a relatively large amount of soap is used so that the resin is spontaneously emulsified.

Applying Emulsions as Surface Coatings

Emulsions have the same penetrating characteristics as aqueous coatings in that they tend to swell the fibers in the paper. This reduces the effective pore size of the paper and, in some cases, causes curling and warping. The viscosity of the emulsion and the droplet size determine the penetrating properties. The viscosity of the resin in the lacquer phase is also a factor; it has been reported that a given resin penetrates paper at the same rate, whether applied as a lacquer or as an emulsion.[63]

In order to obtain a continuous film with good water and water-vapor resistance, it is necessary that the dispersed droplets in the emulsion coalesce on drying. The solvent in the lacquer phase is responsible for this after-flow, and consequently most of the solvent must be retained in the film until the water is evaporated or absorbed by the paper in order for this after-flow to take palce. In order for this to take place, the ratio of water to solvent in the lacquer must not be too great. Heating of the coated paper to a high temperature is effective in fusing the coating.

Types of Aqueous Emulsions

Polyvinyl acetate emulsions can be readily prepared by dissolving the resin in a water-immiscible solvent, incorporating an emulsifying agent, and then emulsifying in water of low mineral content under violent agitation. The emulsion can be improved by passing through a homogenizer or colloid mill. From 0.5 to 5.0% of emulsifying agent (ammonium oleate, triisopropanolamine oleate, or sodium lauryl sulfate) gives the best results. A suitable formula is:[64]

82% Lacquer phase	50.0% polyvinyl acetate resin 5.0% tricresyl phosphate 43.5% toluene 1.5% oleic acid
18% Water phase	8.0% ammonia (28%) 92.0% distilled water

Polyvinyl acetate-chloride copolymer resins can be prepared in emulsion form by the same general procedure.[65] Emulsifying agents such as the sodium salts of alkyl naphthalene sulfonic acids or ammonium oleate can be used. If the resultant film is to be air-dried, the concentration of resin in the lacquer phase should not exceed 25%. However, if the film is to be dried at a high temperature, a gel type of emulsion may be used containing a high percentage of resin dispersed in a non-solvent thinner. In this case, the dispersed particles of resin do not merge into a continuous film until the film is heated to a high temperature.

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[63] C. B. Hollabaugh, *Paper Trade J. 101,* No. 25: 347–353 (Dec. 19, 1935)

[64] Technical Bulletin, "Vinylite Vinyl Acetate Resins," p. 10, Bakelite Corp., Carbide and Carbon Corp., New York, N. Y. (1947)

[65] Technical Bulletin, "Vinylite Resins," Bakelite Corp., Carbide and Carbon Corp., New York, N. Y. (July, 1948)

Prepared emulsions of polyvinyl acetate resin are sold commercially. An analysis of one commercial product is as follows:[65]

Total solids, % by weight	50
Viscosity, centipoises	3,000
Free monomeric vinyl acetate, % by weight	1.5
*p*H	4.5 to 5
Viscosity of contained resin[a]	100 to 150
Average weight, pounds per gallon at 60° F.	9.25
Particle size, average maximum	Not over 10 microns

[a] The viscosity in centipoises at 20° C. of 86.1 g. vinyl acetate polymer plus benzene to make one liter.

Vinyl acetate emulsion can be applied by brush, spray, dip, knife, or roll coaters. The dispersion has good stability to agitation, to brushing, and to dilution with water, and does not show the objectionable stringing that is characteristic of solution coatings of polyvinyl acetate. The *p*H may be adjusted to 7.0 or slightly above by the addition of ammonia or triethanolamine, but excessive amounts of alkali, acid, or inorganic salts should be avoided. Plasticizers may be stirred into the dispersion, and their use in moderate amounts tends to improve the water resistance of the dried film. Concentrations of 10 to 30% (based on the resin) are suggested. Air-dried films are water sensitive, but a short bake (5 minutes at 300° F.) helps to render them water-resistant.

Films of vinyl acetate emulsion are quite resistant to blocking and surface marring, even at high temperatures. The block point is generally about 400° F. (1 p.s.i. for 1 minute), and the print point (temperature at which the coated paper shows the pattern of a piece of cheesecloth placed on the surface for 15 minutes under a pressure of 1 p.s.i.) is about 200 to 220° F.[66] The high blocking resistance naturally hinders heat sealing of the dried film, but excellent bonds can be obtained if the surfaces to be adhered are coated and then pressed together while still damp. Force drying or baking and the application of pressure improve the strength and resistance of the bond. If it is not practical to seal the surfaces within two or three minutes of application of the film, addition of ethylene glycol or other suitable material will extend the period of dampness of the coating. Films which have not dried more than a few days and have not been baked can be reactivated for heat sealing by merely wetting the surface with water or weak ammonia.

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[66] Technical Bulletin "Vinylite Resins," Bakelite Corp., Carbide and Carbon Corp., New York, N. Y. (July, 1948)

There is available a commercial polyvinyl acetate powder which can be dispersed in water to form an emulsion suitable for coating paper.[67] The powder is readily dispersible in water in widely varied ratios to give dispersions ranging from low viscosity hydrosols to thick pastes. To prepare an emulsion, the dry powder should be slowly added to water with mild agitation. Dispersion is complete when no lumps are present in the emulsion. The dispersions may be treated with amines (such as triethanolamine) to enhance heat-sealing properties or to adjust the *p*H, with little or no danger of discoloration.

Polyvinyl chloride resins are available as emulsions in several different forms (see Ch. XXIII). Synthetic rubber latices are also available (see Ch. XXIII).

Polyvinylidene chloride-polyvinyl chloride copolymer emulsion (Saran) (see Ch. XXIII) can be applied to paper by knife or roll coater to produce a coating which is heat-sealing, water-repellent, oil-resistant, and water vapor-resistant.[68] A suitable formula is:

100 parts commercial latex (57% solids)
24 parts dibutyl phthalate emulsion (60% solids)
1.7 parts thickening agent

The coating must be dried in a festoon or tunnel drier because of its tacky nature.

Ethylcellulose emulsions may be prepared by emulsifying ethylcellulose lacquer in water. The ethylcellulose is first dissolved in xylene or naphtha and a solution of emulsifying agent in water is then added slowly to the lacquer with thorough stirring. At first, a water-in-oil emulsion is obtained, but this reverses to an oil-in-water emulsion at the point of water saturation. Soft water should be used, and the emulsion should be passed through a colloid mill. A suitable formula is given below.[69]

Lacquer phase	Ethylcellulose	27
	Plasticizer	9
	Xylene	51.2
	Butanol	12.8
Water phase	Water (*p*H 8.0 with ammonia)	49.5
	Emulsifying agent	0.5

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[67] Technical Bulletin "Vinylite Resins," Bakelite Corp., Carbide and Carbon Corp., New York, N. Y. (July, 1948)

[68] G. W. Stanton and W. A. Henson, *Paper Trade J. 123,* No. 6: 68–72 (Aug. 8, 1946)

[69] Technical Bulletin, "Dow Coating Materials, Ethocel," The Dow Chemical Co., Midland, Michigan (1947)

Acrylic resin emulsions are available commercially in solids content ranging from 25 to 50%. The solutions vary from water white to slightly yellow in color. Films produced from acrylic resin emulsions range from hard, brittle films with good surface slip to elastic, flexible films which are quite tacky, depending upon the grade of resin used. The films have good resistance to aliphatic hydrocarbons, mineral oils, alkalies, and acid. The film is fairly water resistant if baked or force-dried at temperatures above 110° C.

Aqueous emulsions of nitrocellulose lacquer have been suggested for paper coating.[70] These produce thin, continuous, non-porous films on paper. Polyvinyl butyral emulsions produce coatings of excellent properties, but have the disadvantage of high cost. Polystyrene emulsions are suitable for coating paper if the coatings are force-dried at 100 to 150° C.

Organosols and Plastisols

Organosols and plastisols constitute a different class of emulsions. Organosols consist of a dispersion of resin in a plasticizer and a non-solvent liquid (i.e., diluent). Plastisols consist of a dispersion of resin in a non-solvent plasticizer without diluent.

Vinyl chloride-acetate copolymers are used in making organosols and plastisols. The resins used for this purpose contain a very high ratio of vinyl chloride and have a high molecular weight. Other resins may be added, such as the rosin-derived alkyds (Neolyn resins), to improve the adhesion characteristics and the gloss of the film. Organosols may be prepared by mixing the ingredients in a slow speed agitator or by milling in a ball mill for twenty to forty hours, depending upon the form of the original copolymer. Resin, plasticizer, diluent, and stabilizer are mixed together until a smooth creamy paste containing particles about 0.2 micron in size is obtained. Generally, from 30 to 100% plasticizer on the weight of the resin is used.

One advantage of organosols and plastisols is that relatively cheap diluents, such as aromatic, naphthenic, and aliphatic hydrocarbons are used. Another advantage is that dispersions of high solids can be prepared using resins which normally form solutions of very high viscosity. Organosols containing up to 60 to 80% non-volatile components have been prepared, and plastisols up to 70 to 100% solids are used with no volatile ingredients at all. These high solids permit the application of very heavy coatings.

The diluents and plasticizers in organosols and plastisols exert very little solvent action on the resin at room temperature. However, when the film is heated to high temperature, the diluents and plasticizers act as solvents for the resin and cause the resin to fuse into a continuous coating.

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[70] C. B. Hollabaugh, *Paper Trade J. 101,* No. 25: 347–353 (Dec. 19, 1935)

Plastisols have higher fusing temperatures than organosols because of the higher molecular weight of the resins used, and because there is no diluent to solvate the resin during heating. In baking organosol coatings, an initial bake for thirty to sixty seconds at 200 to 250° F. is used, followed by a bake of ten to thirty seconds at 350 to 400° F. As a rule, the first section of the oven is steam-heated and is equipped for the recovery of solvent vapor, while the final section is usually heated by electrical heaters or indirect fuel heaters. The coatings have good abrasion resistance and good flexibility because of the high molecular weight of the resins used. As a rule, the heat-seal properties are not so good as with other types of coatings.

Coating with Hot Melts

Hot-melt coating involves the application of molten wax or resin to the surface of the paper, followed by cooling to produce a smooth, hard film on the paper surface. Waxing of paper is an example of a hot-melt coating process which has been used for years. Recently, advances have been made in the number of materials suitable for hot-melt application.

Hot-melt coatings are of two types: (*1*) those consisting of wax alone, or a mixture of wax with a small percentage of modifying material, such as polyisobutylene or cyclized rubber; and (*2*) those consisting principally of a film-forming resin and relatively small percentages of modifying agents, such as wax, non-film-forming resin, and a plasticizer. Hot-melt coatings have the advantage of low cost, low fire hazard, and quick drying, and the coatings are heat sealing.

Heating of the melt in the bath is done by electrical heaters or by circulating oil. Controls must be adequate to maintain the temperature within 8 to 10° F. Temperatures differ widely, depending upon the type of melt used. For the sake of convenience, it is possible to make an arbitrary distinction between high- and low-temperature melts, depending upon whether the melt is applied at a temperature higher or lower than 300° F. Most hot melts are applied at a temperature between 225 to 350° F. The temperature must be high enough to keep all the ingredients in solution, since otherwise a streaky coating will be obtained. Temperatures as high as 400° F. are sometimes used, but in general, high temperatures are to be avoided, since they cause drying out and a weakening of the paper. In cases where high temperatures are required, it is desirable to run the machine at high speeds and to pass the paper over cooling rolls immediately after coating to prevent too long a contact at high temperature.

Methods of Applying Hot Melts

Hot melts can be applied by roll, knife, dip, spray, or extrusion coaters. One of the most popular types of roll coaters is the gravure coater. One model suitable for low-viscosity melts consists of a heated gravure roll which revolves in the hot melt, a doctor blade for removing excess melt from the roll, and a pressure roll for holding the paper web against the gravure roll. Another model suitable for higher viscosity materials contains a third roll, a hot metering roll which contacts the pick-up roll and controls the quantity of melt applied to the paper. The melt is applied in the form of a pattern, and hence must be smoothed out by passing the coated paper under a heated smoothing bar. The smoothing bar remelts the coating in the high spots and causes it to flow into a smooth film.

After the coating is smoothed, it must be cooled rapidly. Low-temperature melts need to be chilled to produce a glossy surface,[71] but high temperature melts generally have gloss characteristics of their own. If the coating is cooled too slowly, it tends to crystallize or separate and form a non-glossy coating. The rate of cooling affects the size of the wax crystals, and this influences the water vapor resistance of the coating.

Paper for hot-melt coating must not be too porous, because this results in excessive penetration and the loss of protective qualities. The amount of melt required for different papers has been given by Viner and Miller as follows:[71]

Type of paper	Pounds of melt per ream
Glassine	2–3
Book	4–6
Wrapping or bag	8

Generally speaking, about 6 to 8 lb. of hot melt per ream are required for good quality supercalendered papers. For heat sealing, about 8 to 10 lb. of coating are required. Special papers for packaging frozen foods may require 10 to 30 lb. of coating.

Waxing with Paraffin

Waxing with paraffin dates from about 1866 and hence is one of the oldest hot-melt coating processes. Paraffin is popular because of its relatively low cost, low melting point, low viscosity, and ability to produce films which are hard, glossy, non-tacky, and water-resistant.

Paraffin wax occurs naturally with crude paraffin oils, and is removed from distillate stocks to lower the pour points of these oils. It is derived from the waxy overhead fraction known as the wax distillate, which is obtained in the first distillation of the crude oil. Separation is based upon the differences in solidification points between the wax and other components. The first step consists of chilling, after which the mixture is filtered through a filter press where the solid wax is removed. This wax, which is known as slack wax, has a very high oil content, and must be put through another operation, referred to as sweating. This consists of chilling to produce a solid cake and then slowly raising the temperature to sweat out the oil. The remaining wax, which is known as crude scale wax, finds more use in the paper industry than slack wax, but its use is limited because of the 1 to 5% oil which it contains. This oil imparts odor to the wax and lowers the strength and hardness of the wax.

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[71] J. W. Viner and B. C. Miller, *Paper Trade J. 118*, No. 24; 221–222 (June 15, 1944)

Refined waxes are made by additional sweating operations which resolve the wax into various fractions. Fully refined waxes are made by a solvent pressing operation, which is substantially a recrystallization of the wax from a suitable solvent. This produces a wax of very low oil content (less than 0.5%). The final steps in the treatment of fully refined wax include a steaming operation to remove odor and a final decolorization by filtering through fuller's earth or bone char. In some cases, semi-refined waxes are sold, but these are poorly defined and samples of these grades have shown oil contents ranging from 0.5% to as high as 5.0%, depending upon market conditions.

Paraffin wax is a true member of the paraffin family, being composed of a mixture of straight-chain saturated hydrocarbons ($C_{23}H_{48}$ to $C_{35}H_{72}$). The various fractions have different melting points, the lowest molecular weight fraction having a melting point of about 30° C. being liquid at ordinary room temperature. The melting point of commercial paraffin is generally between 120 to 130° F., although paraffin ranges from 110 to 150° F. in melting point. (The melting point of paraffin is determined as the temperature at which melted paraffin first shows a minimum rate of temperature change when cooled slowly under prescribed conditions.) Melted paraffin has a very low viscosity, the viscosity being very nearly the same as the viscosity of the oil from which it was derived (as shown by comparative viscosities at 210° F.). Paraffin is crystalline in nature and forms films which tend to crack and check. Chlorinated paraffins are also manufactured. These range from pale viscous liquids of about 42% chlorine content to yellow solid resins of about 70% chlorine content.

A considerable amount of paraffin wax (almost 80% of the total production) is used in the paper industry. Machine-finished papers, supercalendered papers, coated (titanium dioxide) papers, glassine, and greaseproof are some of the grades used for waxing. The waxed products are used for bread wrappers, drinking cups, bottle-cap stock, and paper cartons. The stiffening effect of paraffin on paper is related to the modulus of rupture of the wax.[72] Paraffin produces a brittle film at low temperature, and hence is not suitable for frozen food wrappers if the wrapper is to be folded, although plasticizers (e.g., aluminum stearate) can be added to improve the flexibility of the film. The film softens at a relatively low temperature, and hence the waxed product should not be stored in a warm place.

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[72] L. E. Hoag, *Tappi 33,* No. 7: 343–345 (July, 1950)

Difficulty is sometimes encountered with a loss in hardness and the development of odor in the wax caused by a chemical reaction between the wax and the oxygen in the air. To minimize these effects, the temperature in the wax bath should be as low as possible (not over 215° F.), and low temperature steam should be used for heating. In addition, the wax bath should be designed so that a minimum of area is exposed to the air. The system should be cleaned regularly. Paraffin can be stored indefinitely in liquid form at temperatures below 150° F., for about three to four weeks at 150° F., for several days at 200° F., but only for a few hours at 250° F.[73] Anti-oxidants may be added to the wax. The efficiency of anti-oxidants can be tested by passing oxygen at a controlled rate through a sample of the wax at 160° C. The results can be expressed as the number of hours required to yield a peroxide number of 50. In some cases, dark-colored insoluble products are produced in the wax which are caused by a reaction between the molten wax and metal. Copper is particularly bad in this respect, and consequently copper equipment should not be used.

Dry Waxing. There are two types of waxing processes, wet and dry waxing. In dry waxing, the wax is applied in such a way that it is confined entirely within the sheet. Dry waxing is in reality a saturating process.

The wax can be applied by squeeze roll coater or by spraying. The amount of wax applied depends upon the speed of the machine, density of the paper, temperature of the wax, and pressure at the squeeze rolls.[74] According to Ferguson,[75] the speed of the paper should be the same as the peripheral speed of the rolls. Soft rubber squeeze rolls should be used where a high percentage of wax is desired. The temperature of the wax should be relatively high, and the squeeze rolls should be heated to drive wax into the paper. A heated roll may be used after the squeeze rolls to drive wax farther into the sheet. A chilled finishing roll may be used to cool and set the wax.

The paper used for dry waxing should have a low, but even, finish. The moisture content should be between 6 to 8%. Over 10% wax must be applied to obtain uniform results. The upper limit is between 20 to 25% wax, although most commercial papers contain about 16 to 20%.

Dry waxed papers do not present a continuous film of wax because most of the wax exists within the sheet, and very little is left on the surface of the paper. Consequently, uncoated fibers protrude above the surface of the sheet. These fibers are free to absorb moisture and, as a result, dry waxed papers have very little resistance to water vapor. On the other hand, dry waxed papers have a high degree of resistance to liquid water because the pores of the paper are filled with wax.

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[73] W. S. Bondy, *Paper Trade J. 129*, No. 12: 78 (Sept. 22, 1949)

[74] R. B. Killingsworth, *Paper Mill News 66*, No. 25: 70, 72 (June 19, 1943)

[75] E. E. Ferguson, *Paper Ind. 28*, No. 7: 979–984 (Oct., 1946)

The absorptiveness of paper for paraffin can be measured by placing a weighed sample of the paper to be tested between two sheets of waxed blotting paper, and inserting between two steel or glass plates, and heating the assembly at 105° C. for one hour. The difference in weight before and after treatment is a measure of the absorptiveness of the paper for paraffin. The amount of paraffin absorbed is reported as a percentage of the unwaxed paper to the nearest one per cent. Waxed blotters can be prepared by immersing samples of blotting paper in molten paraffin (71° C.) for thirty minutes and then drying in an oven (105° C.) for one hour.

A rapid test for measuring the wax absorptiveness of paper can be carried out by soaking samples of the paper in a bath of hot paraffin (130–132° F.) for twenty seconds and then, after cooling, scraping the hardened wax off the surface of the paper, using the edge of a microscope slide. The percentage of wax absorbed is determined by the difference in weight between the paper before and after waxing.

Wet Waxing. In wet waxing, the wax film is kept as much as possible on the surface of the paper. The final product is called self-sealing paper because the paper can be readily sealed with heat on automatic wrapping machines. Wet-waxed papers are more water-repellent than dry-waxed papers, and furthermore, have a high degree of water-vapor resistance because of the film of wax on the surface of the paper. The wax load may be 40 to 50% of the weight of the base paper.

Roll or spray coaters can be used, or if both surface and internal wax is desired, the sheet may be submerged in molten wax at 150 to 215° F. Wire-wound steel rods are also used. After waxing, the paper is passed over refrigerated rolls to set the wax or, if minimum penetration and maximum gloss are desired, the wax may be applied at low temperature and the waxed sheet quenched by dipping in water or brine at about 40° F. This produces a higher gloss than passing over chilled rolls, because of the more rapid cooling of the wax. Water is removed by blowing, suction, scraping, or squeezing.

Waxing stock for self-sealing papers should have a high machine finish to prevent excessive penetration of wax. The moisture content is usually higher than that for dry waxed papers and is usually between 7 to 9%. The paper should be clean, since dirt in the paper shows up more after waxing. Glassine papers are used where the highest transparency and greatest protective qualities are desired. Waxes with melting points lower than 128 to 130° F. should not be used for wet waxing because of the danger of excessive softening of the wax film in warm weather.

When waxing printed papers, trouble is sometimes experienced with bleeding of ink into the hot wax. The amount of bleeding depends upon the type of pigment and vehicle in the printing ink.[76] If the ink contains a drying oil base which has been well oxidized, i.e., dried for a period of twenty-four to forty-eight hours, the ink will be insoluble in the wax. Papers printed with moisture-set inks can be waxed about two hours after printing. If the ink has been modified with wax-soluble resins, it will tend to bleed. Inks dispersed in petroleum hydrocarbons will tend to dissolve off the sheet.

Waxing of Paper Cartons. In addition to the waxing of paper, wax is also used for the waxing of fabricated paper cartons. This may be done by (*1*) prewaxing of the package before filling or (*2*) waxing of the package after filling by shower method, single-dip coating, or by double-dip coating. In the prewaxing process, the paper carton (with glued bottoms) is immersed into the wax bath and then drained. Later the package is filled and the top is sealed. Applying wax to the filled carton is a more foolproof method, and generally a dipping is used. In the single-dip method, the entire package is submerged in molten wax. In the double-dip method, the package is coated half at a time. The time of contact of the paper with the wax should be carefully regulated. If submerged in the hot wax too long, the air in the box is greatly expanded, causing bubbles to form in the wax film. Too short a period of contact is also bad, because this results in a poorly bound coating, due to the congealing effect of the cold package on the film of wax. In the double-dip method, there is less danger of bubble formation, since the wax is applied to only half of the package at a time.

Determination of Paraffin in Waxed Papers. The amount of paraffin in waxed papers can be determined by extracting folded strips of the paper with carbon tetrachloride, treating the extract with alcoholic potassium hydroxide, and shaking with petroleum ether in a separatory funnel. The weight of material in the ether extract gives the amount of paraffin in the paper. This test is based upon the assumption that the unsaponifiable material soluble in petroleum ether represents the paraffin content of the paper. The test is therefore not suitable for papers containing materials other than paraffin which has these characteristics.

Waxing with Microcrystalline Wax

Microcrystalline wax is a special grade of hydrocarbon wax derived from petroleum oils. Microcrystalline waxes were first introduced about 1927, and since then, have supplemented paraffin wax for many uses. They vary from plastic products to hard, and even brittle products.

Petrolatum is the raw material source of microcrystalline waxes. It is obtained from the heavy lubricating oils after the solvent refining of paraffin oil. In other words, petrolatum is removed from heavy lubricants to lower the pour point of these oils, and is therefore comparable to slack wax in paraffin operations. In preparing microcrystalline wax, the petrolatum is subjected to a de-oiling operation to produce waxes of controlled melting points and different degrees of hardness. The waxes are dark tan to brown in color, but white or lemon-colored waxes can be obtained by decolorization with activated clays or bone char.

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[76] E. F. Carman, *Paper Ind. 27,* No. 9: 1367, 1371 (Dec., 1945)

At one time, microcrystalline waxes were believed to be amorphous, but are now known to contain very fine crystalline material much finer than the crystals in paraffin wax, hence the name "microcrystalline wax." The exceeding small crystal structure is believed to be due to the presence of a crystal inhibitor, which is not present in paraffin wax.[77] Microcrystalline waxes generally contain a high proportion of oil, which has a strong affinity for the wax and controls the hardness and penetrating qualities of the wax. Microcrystalline waxes differ further from paraffin wax in having higher molecular weight, higher melting point, and higher viscosity in the molten state. The melting point varies from 150 to 200° F., and the waxes are generally classified as follows:

High melting	175° minimum
Medium melting	166° minimum
Low melting	155° minimum

In general, the lower melting point waxes are the cheapest.

Microcrystalline wax is not hard enough to be used by itself for most coating purposes, but it is often used in combination with paraffin to increase the flexibility and toughness of the film. Papers coated with paraffin-microcrystalline wax retain their water-vapor resistance even after considerable handling. There is practically no difference in the water-vapor resistance of paraffin and microcrystalline wax coatings so long as neither film is folded, but paraffin-coated papers lose their vapor resistance as soon as they are folded, whereas papers coated with microcrystalline wax do not.[78] Coatings containing microcrystalline wax have improved heat-sealing properties and increased oil resistance. Because of its greater oil resistance, microcrystalline wax is used in coatings for butter, lard, and cookie cartons. The grease resistance increases with the melting point of the wax, and since microcrystalline waxes have higher melting points than paraffin, they are only about one twenty-fifth as soluble in fats as refined paraffin (melting at 130° F.). Microcrystalline wax is used mostly in wet waxing, but is sometimes used in dry waxing when grease resistance is desired.

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[77] B. H. Clary, *Paper Ind. 27,* No. 11: 1679–1682 (Feb., 1946)

[78] *Idem.*

The ductility of the film is roughly proportional to the amount of microcrystalline wax in the blend. In making frozen food wrappers, it is customary to use 25% microcrystalline wax and 75% paraffin, but up to 50 to 60% microcrystalline wax is sometimes used. However, above about 25% microcrystalline wax, the effects of increased tackiness and tendency to block become apparent.

Use of Resin-Wax Blends as Hot Melts

Resins are used in combination with waxes to improve the properties of the film. In some cases, only a small amount of resin is used, in which case the resin acts as a modifying agent for the wax. In other cases, the melt is predominantly resin.

Film-forming resins (e.g., ethylcellulose and polyethylene) are widely used to impart blocking resistance and toughness and to increase the heat resistance of the film, although certain film-forming resins lack sufficient heat stability to be used as hot melts (e.g., nitrocellulose and polyvinyl chloride). Non-film-forming resins (e.g., modified rosin derivatives, modified phenolics, and modified alkyds) are sometimes added to increase gloss, transparency, water and grease resistance, and adhesion of the film. Oxidizing or polymerizing resins are, in general, unsuitable for hot melts because of separation on heating. Cyclized rubber and polyisobutylene add flexibility and increase the adhesiveness of the wax film, but they blend with wax with some difficulty. As a general rule, resins used in hot melts should show no decomposition at temperatures 50° F. or more above the temperature of application of the melt.

Resin-wax melts may contain added ingredients such as oils, metallic soaps, non-volatile solvents, and plasticizers, which are added either to improve the working properties of the melt or to improve the properties of the film. These ingredients must be compatible with both the resin and wax, and must not separate on heating. Other waxes, e.g., carnauba, ozokerite and some of the synthetic waxes, may be used in conjunction with paraffin to increase the hardness, tensile strength, and gloss of the film.

Use of Ethylcellulose. One of the most important cellulose derivatives for hot-melt coatings is low-viscosity ethylcellulose. Ethylcelullose has too high a melting point to be used by itself, and consequently is always used in combination with other materials. In blends with paraffin, ethylcellulose adds toughness, flexibility, and block resistance to the film. The wax provides water and water vapor resistance.

Ethylcellulose is not compatible with paraffin by itself, and consequently a third ingredient is necessary to act as a mutual solvent. Hydrogenated vegetable oils (e.g., castor oil) are best suited for this purpose. Non-film-forming resins are sometimes added to increase the hardness, to add gloss, and in some cases, to improve the adhesion and water resistance of the film. Resins of high acid number should not be used. Plasticizers are added to improve the flexibility.

In preparing the melt, all ingredients except the ethylcellulose are melted together, after which the ethylcellulose should be added gradually. The melt should be heated to 300 to 325° F. until all air bubbles are removed. Several examples of formulas for ethylcellulose hot-melt coatings are given below.[79]

Formula	Coating for				
	Soap wrap, shelf paper, and label papers	Bread wrap	Frozen food wrap	Low moisture vapor transmission	High grease resistance
Ethylcellulose	15	10	20	20	30
Resin	35	18	40	20	28
Plasticizer	5	None	None	None	4
Paraffin wax	25	28	14	32	14
Vegetable wax	20	44	14	28	24
Microcrystalline wax	None	None	12	None	None

Another formula for a hot-melt coating is as follows:[80]

Ethylcellulose (10 centipoises)	11.5
Amberol (maleic rosin type phenol-formaldehyde resin)	33.3
Paraffin wax (140° F.)	19.0
Opal wax No. 10	20.0
Blown castor oil	15.7
Triphenyl phosphate	0.5

In preparing this mixture, all ingredients except ethylcellulose should be melted together and heated to 130 to 150° C. The ethylcellulose should then be sifted in as fast as it will dissolve. Bleeding an inert gas into the mixture from the bottom of the pot helps to maintain best color. The higher the percentage of ethylcellulose in the formula, the higher the viscosity of the melt.

Ethylcellulose hot melts can be applied by roll, knife, or spray coaters, or by dipping. The melt is usually applied at a temperature of 230 to 275° F. At temperatures lower than 230° F., the ingredients are likely to separate. On the other hand, prolonged heating at high temperatures causes some degradation and loss of film flexibility. Anti-oxidants help to stabilize the melt. On a good quality supercalendered paper, about 5 to 8 lb. of ethylcellulose hot melt will produce a coating of good gloss and protective qualities.

Use of Polyethylene. Polyethylene is not widely used alone in hot melts because of its high viscosity. However, polyethylene of relatively low molecular weight (i.e., about 12,000) can be used alone or in combination with waxes. The coating is usually applied by extrusion coater in a film about ½ mil in thickness. Coverage is high because of the low specific gravity. The film has a very high degree of flexibility and shows an enormous elongation at a load just below the breaking point. The water vapor resistance is high, but the resistance to carbon dioxide and oxygen is low. The coated paper is admirably suited for use as a locker paper for wrapping frozen foods. The coating can be heat sealed at 325 to 350° F.

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[79] Technical Bulletin, "Ethocel Hot Melts for Paper Coatings," Plastic Division, The Dow Chemical Co., Midland, Michigan (1948)

[80] Private communication, p. 49, Rohm and Haas Co., The Resinous Products Div., Philadelphia, Pennsylvania (Apr., 1948)

Papers coated with polyethylene-wax blends show good strength, excellent flexibility, good heat-seal properties, good electrical properties, and high water-resistance. The addition of 2 to 5% of polyethylene resin to paraffin increases the blocking temperature, reduces rub-off, increases the tensile strength, and improves the strength of heat-seal bonds. The water vapor resistance is not appreciably reduced. The resin increases the viscosity of the wax and necessitates the use of a slightly higher temperature. Ordinarily, the minimum temperature will be approximately 212° F. Antioxidants are recommended to prevent oxidation. In the case of microcrystalline waxes, about 1 to 2% polyethylene is helpful in reducing tackiness of the film.

Use of Other Resins. Many of the vinyl resins are not suitable for hot melts because of their tendency to decompose at high temperatures. However, polyvinyl acetate can be used if compounded with natural resins (e.g., dammar) and suitable plasticizers. As a rule, the acrylics and polystyrene resins are not suitable. However, *n*-butyl methacrylate has been used in combination with paraffin, hydrogenated castor oil, and a plasticizer.

Cellulose acetate is not particularly well suited for hot melts because of its low compatibility with resins and plasticizers, although some cellulose acetate has been used. Cellulose acetate butyrate has been suggested for hot melt coatings.[81] Esters having a high butyral content (50%) can be applied at temperatures in the range of 325° F. The following formula has been found satisfactory:[82]

Cellulose aceto-butyrate	40–60%
Resin (e.g., chlorinated diphenyl or rosin-maleic resin)	10–30%
Plasticizer (e.g., dioctyl phthalate, dibutyl sebacate, or *n*-butyl stearate)	15–25%
Wax (e.g., paraffin)	1–5%

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[81] M. Salo and H. F. Vivian, U. S. 2,387,773 and 2,387,774 (Oct. 30, 1945); 2,409,985 and 2,409,986 (Oct. 22, 1946); 2,410,685 (Nov. 5, 1946)

[82] W. S. Penn, *World's Paper Trade Rev. 128*, No. 7: 41–44 TS (Aug. 14, 1947)

Use of Rubber Derivatives in Hot Melts. Natural rubber is not well suited for hot-melt coatings, although it has been suggested in combination with paraffin.[83] As mentioned earlier, cyclized rubber can be used in mixture with paraffin to improve the flexibility, toughness, and gloss of the film, and to strengthen the heat seal.[84] This product is soluble in paraffin to a slight extent at room temperature and is completely soluble in all proportions at a temperature above the melting point of the wax.[84] It raises the melting point of the wax approximately 3° F. for every 5% of rubber and also increases the viscosity of the melt. Generally by the time sufficient cyclized rubber is incorporated in paraffin to obtain greatly improved flexibility, the mixture is so viscous that it is difficult to handle with conventional waxing equipment.

Of the synthetic rubbers, the isobutene rubbers and butyl rubbers are most interesting. These can be used in hot melts in combination with wax to improve the flexibility and heat-seal properties of the coating.

Carbon Paper

Carbon paper is made by coating paper with a mixture consisting principally of a wax and a pigment. The color is obtained from the pigment, usually a carbon black of low oil absorption, plus toners, usually lake pigments or oil-soluble dyes, which are added to increase the blackness. The wax, which acts as a binder for the pigment, must have a viscosity low enough to permit slight penetration into the paper, but not so low that the wax strikes through or sweats oil. Waxes with a melting point between 105 to 120° F. and a viscosity of about 60 or 70 Saybolt at 210° F. are generally used. The principal wax used is carnauba, although some ceresin, beeswax, candelilla, ozokerite, ouricury, and synthetic waxes are also used. Special grades of microcrystalline waxes may be added to soften the coating and improve the printing qualities. In addition to the above ingredients, non-drying oils (mineral oils) are used to soften the coating and control the amount of coating transferred to the copy. Oleic acid is sometimes used as a solvent for oil-soluble dyes.

All carbon papers must be free of offset, flaking, wrinkles, curl, or other defects, and must give a good impression on the copy paper. The coating must be hard enough not to smear in hot weather, but the exact degree of hardness depends upon the intended use, that is, whether the paper is designed as a pencil carbon, a typewriter carbon, or a one-time carbon. The amount of coating varies from a very thin coating used in making one-time carbons to a very heavy coating used in making high-grade typewriter carbons for multiple use. The latter, in which the paper may be reused up to 40 to 50 times, must have a coating of very high color value and the coating must be compounded so that only a small amount is transferred to the copy sheet. A simplified formula for a typewriter carbon would be as follows:

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[83] A. Abrams and C. L. Wagner, U. S. 2,054,112 and 2,054,113 (Sept. 15, 1936)

[84] H. R. Thies, *Paper Trade J. 108,* No. 8: 79–84 (Feb. 23, 1939)

Carnauba wax	34%
Ozokerite	6%
Beeswax	7%
Petrolatum	6%
Mineral oil	25%
Carbon black	13%
Toners	6%
Oleic acid	3%

In the coating of carbon paper, the molten wax mixture is applied to the paper at a temperature of about 200° F. Coating is done on a carbon paper coater which consists of an inking roll which is supplied with coating directly from a bath or from a heated fountain. The inking roll revolves in a direction opposite to that of the paper web. Excess coating is scraped off the paper by an equalizer rod and the sheet then passed over a water-cooled cylinder to chill and harden the coating. Crystallization of the wax occurs upon chilling, and this process continues over a period of several days. For this reason, it is customary for carbon manufacturers to age their coated paper for two to seven days before shipping.

It is absolutely essential that the coating be absorbed evenly by the paper. Therefore, the paper must have a smooth surface, uniformly high density, good formation, and above all, be free of pinholes. Further requirements are high strength, low basis weight, and freedom from flaws such as slime spots and dirt specks. Because of these rigid requirements, the base stock for carbon tissue is difficult to make. The best grades are made from new cotton or linen rags, or from manila hemp, whereas the cheaper grades are made from sulfate and sulfite pulps. The stock is beaten for a considerable period of time, often up to thirty hours, in order to develop maximum strength. The stock is only lightly sized. Calcium carbonate is often used as a fller, but the ash should not be over 5%. The basis weight is usually 4, 5½, 7, or 10 lb. per ream (20 × 30—500). The 4-lb. paper is used when a large number of copies is to be made; the 5- and 7-lb. papers are suitable for ordinary work.

In addition to the grade of carbon tissue described above, there is another grade known as carbonizing paper. This is a heavier paper which is made in basis weights of 14 to 20 lb. (17 × 22—500). It is used mostly in sales books which are intended for pen and pencil work. Bleached and unbleached sulfite and groundwood are generally used in making the base stock, which must be dense enough to keep the wax coating on the surface of the paper, and must be high enough in opacity to prevent the coating from showing through. Generally, a thicker film of coating is used in this grade than in the typewriter grades.

CHAPTER XXIII

RESINS

The general properties of resins are of great importance to the paper chemist because of the wide use of resins in the paper industry. Some of these uses include: (*1*) the use of rosin as an internal sizing agent, (*2*) the application of resin emulsions and latices at the beaters and the calender stacks, (*3*) the lamination of paper with resin solutions, resin emulsions, and hot melts, (*4*) the coating of paper with lacquers and varnishes, and (*5*) the impregnation of paper with resin solutions and latices. In this chapter, the origin and method of manufacture of resins is discussed, together with their general solubility and compatibility characteristics. For specific information on the use of resins, the reader is referred to the chapters on coating with resinous materials, internal treatment of paper with resinous materials, paper plastics, and laminating.

There are several important classes of resins, and these have been divided in this chapter into the following: natural resins, synthetic and semi-synthetic film-forming resins (cellulose derivatives and vinyl polymers), synthetic non-film-forming resins, and rubber and rubber derivatives. The synthetic resins offer a promising field for development and have already replaced the natural resins for most uses.

The synthetic resins are divided into the film-forming and non-film-forming types. Film-forming resins are those which form films of sufficient flexibility and cohesion to be self-supporting. Non-film-forming resins are those which form hard, brittle films which are not self-supporting. The classification is arbitrary and difficult to make, since there is considerable overlapping in properties. For example, many resins which are considered to be film-forming will not form continuous films unless they are compounded with plasticizers and modifiers. On the other hand, some of the non-film-forming types produce films of a fair degree of continuity when properly compounded with modifiers and plasticizers.

The important properties of resins are their chemical characteristics, softening temperature, flow properties, and film-forming characteristics. If sold as a liquid product, the volatile content is important. The solids can be determined by evaporation of liquid resins in an open cup, but this method has the disadvantage that some of the volatile resin-forming material is lost. Another method is to evaporate a sample of the liquid resin at about the same temperature used in curing the resin, with a relatively large surface area exposed. Still another method is to cure the resin by heat or by the addition of a small amount of acid so that all the resin-forming material is solidified.

Natural Resins

Natural resins are obtained, for the most part, as exudations from living trees or plants. The resins are collected and sold with a minimum of chemical and physical treatment. Many natural resins are named after the geographical location of the source of the resin, e.g., East India, Manila, and Congo resins.

At one time the natural resins were the only available resins, but recently they have been largely replaced by the synthetic products. However, some natural resins (e.g., rosin) are still being used in large quantities by the paper industry. Most of the natural resins are used in varnishes and lacquers for coating paper, although rosin is, of course, most widely used for sizing.

Natural resins have many disadvantages, although these disadvantages do not apply to all natural resins. Some of the common disadvantages are lack of adequate supply, fluctuating market price, bad odor, and tackiness of film. On the other hand, natural resins generally have good compatibility with a wide variety of other resins and waxes, and excellent solubility, particularly in alcohol.

Rosin

Wood and gum rosin are the two major classes of this important product of the Southern pine. Both are almost exclusively obtained from the longleaf (*Pinus palustris*) and slash (*P. caribaea*) pines. Gum rosin is a product of the live tree, while wood rosin is obtained from virgin stumps. Through the development of refining techniques, particularly as applied to wood rosin, these rosins have become readily interchangeable for all important commercial applications.

Gum rosin is a component of oleoresin obtained from the living tree by wounding. The oleoresin usually contains approximately 68% rosin, 20% turpentine, and 12% water. The rosin is recovered as a residue after distilling off the turpentine and water. The color of the rosin depends upon the care used in eliminating foreign matter, both prior to and during distillation.

Wood rosin is extracted from virgin stump wood available on millions of acres of cut over land in the southeastern United States. Only the stumps of virgin pine yield sufficient rosin and terpenes to process economically. The extractable material from second-growth stumps amounts to only about 50% that derived from the virgin wood. Extraction is accomplished with such solvents as gasoline and benzol under pressure after the stumps have been chipped and shredded. The solvent extract is fractionated to yield recovered solvent, turpentine, monocyclic terpene hydrocarbons, and pine oil, the crude rosin remaining as a molten residue. This rosin is a dark ruby red color and must, therefore, be refined for general commercial acceptance.

Two refining procedures are employed commercially, solvent refining and adsorbent earth refining. In the former, a gasoline solution of the crude rosin is extracted with furfural to yield a gasoline solution of the pale rosin and a furfural solution of the dark-colored constituents. The efficiency of the solvent extraction determines the grade of rosin recovered. In the adsorbent earth process, a gasoline solution of the crude rosin is passed through active earths, such as fuller's earth, which selectively adsorbs the color bodies, giving an effluent of pale rosin solution. In both instances, the pale rosin solutions are evaporated to yield the refined finished product.

Rosin is graded for color by comparing with standard color cubes. Major sales of both gum and wood rosin are in grades ranging, on an alphabetical scale, from G to X, the latter being the palest grade available. In order of decreasing color, these grades are G, H, I, K, M, N, WG, WW, and X. The particular grade chosen for the sizing of paper depends upon the brightness requirements of the paper. White papers are sized with G rosin or higher.

The composition of gum and wood rosins is approximately 90% rosin acids and 10% resenes. The rosin acids are present in approximately the following proportions for both rosin types:

Abietic and abietic type acids	50%
Dehydroabietic acid	4%
Dihydroabietic acid	15–16%
Tetrahydroabietic acid	16–17%
Dextropimaric acid	16%

Abietic acid has been investigated most extensively. It has the structural formula shown in Figure XXIII-1. The chemistry of the neutral or unsaponifiable portion of gum and wood rosins has not been developed completely. These materials apparently consist of high-boiling hydrocarbons, sterols, and alcohols combined as esters with small quantities of wax.

The *acid number* of rosin can be determined by dissolving the rosin in warm neutral alcohol and then titrating with 0.5 *N* sodium hydroxide to a pink end point with phenolphthalein. The acid number is the number of milligrams of *potassium* hydroxide consumed per gram of rosin.

$$1 \text{ ml. } 0.5\ N\ \text{NaOH} = 28.06 \text{ mg. KOH}$$

The *saponification* number of rosin can be determined by dissolving a small sample of rosin in 0.5 *N* alcoholic potassium hydroxide, and after boiling for 2 hours, titrating with 0.5 *N* hydrochloric acid to a pink end point with phenolphthalein. The saponification number is the number of milligrams of potassium hydroxide consumed by 1 g. of rosin.

The *ester number* is the difference between the saponification number and the acid number.

The *amount of unsaponifiable matter* in rosin can be determined by boiling a sample of the rosin with an excess of 0.5 *N* alcoholic potassium hydroxide for 2 hours in a reflux condenser. The alcohol is evaporated and water is added, after which the water solution is extracted several times with acid-free ether. The amount of unsaponifiable matter is collected in the ether layer where it is evaporated and weighed. Unsaponifiable matter may also be determined by weighing the amount of rosin unreacted upon when boiled under reflux with sodium carbonate solution. The unsaponified rosin is extracted with ether as in the preceding method.

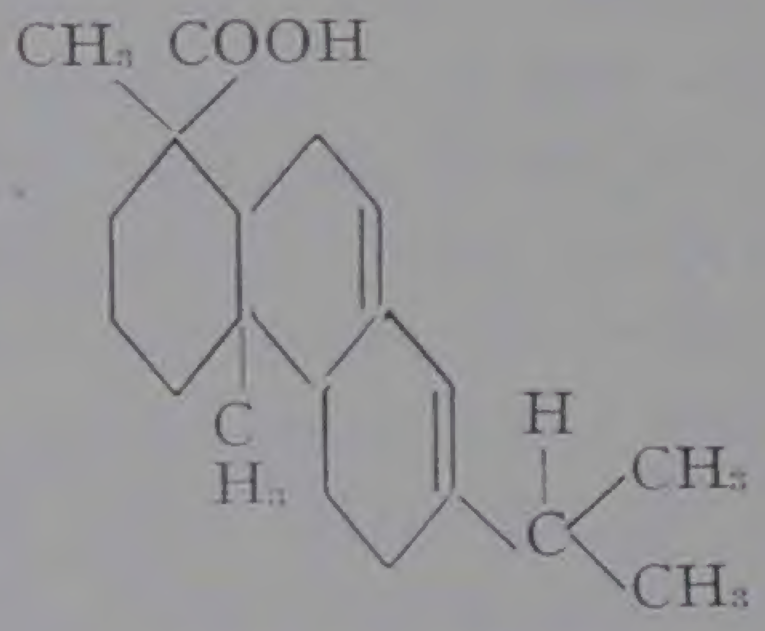

Fig. XXIII-1. Abietic acid.

Other tests sometimes made on rosin are ash and dirt content. Dirt is determined as the matter insoluble in toluene.

Rosin Derivatives

Rosin will undergo most of the normal reactions of organic acids and olefins, such as salt and ester formation, substitution and addition reactions, isomerization, oxidation, hydrogenation, disproportionation, and polymerization. The resin acids containing conjugated double bonds form adducts with alpha-beta unsaturated dicarboxylic acids. Continued heating, with and without catalysts, permits decarboxylation to rosin oils. These same acids are readily polymerized, and polymerized rosins, characterized by melting points ranging from 20 to 30° C. above the normal 80 to 85° C. drop melting point of rosin, are produced commercially (Poly-pale and Nuroz).

Hydrogenation of rosin yields dihydro- and tetrahydroabietic acid, while disproportionation gives dehydroabietic acid and a mixture of dihydro- and tetrahydroabietic acids. Heating to temperatures in excess of 200° C. tends to isomerize rosin, and above 250° C., in the absence of moisture, it is probable that the anhydride is formed. The mixture, termed by earlier investigators "pyroabietic acid," has been more recently identified as a disproportionated product containing the dehydro, dihydro, and tetrahydro acids. Both hydrogenation and disproportionation are used commercially to stabilize rosin and thus prevent oxidation, which results in darkening of rosin with concurrent undesirable changes in its chemical and physical properties.

A wide variety of rosin derivatives are available commercially in both solid and solution form.[1, 2]

The ethylene glycol and diethylene glycol esters of rosin (Flexalyn resins) are important commercial resins which are available as solid resins, as solution of 80% solids, and as emulsions. These resins are soluble in almost all solvents except alcohols, and are completely miscible with mineral and vegetable oils. They are compatible with most other resins, including nitrocellulose, ethylcellulose, rubber, and chlorinated rubber, and are also compatible with a wide variety of waxes, asphalts, and gums. They are used as plasticizers and softeners in resin-coated papers, and as tackifying agents in adhesives, being particularly well suited to making pressure-sensitive adhesives. The emulsions can be used with water-soluble materials, such as starch and casein, to increase the toughness and adhesion, and reduce the water sensitivity of the dried film.

The glycol esters of hydrogenated rosin (Staybelite resins) are very stable derivatives, having an oxygen pick-up of less than 0.5 to 1.0%, compared with over 6.5% pick-up for rosin.[3] These resins are soluble in aromatic hydrocarbons, aliphatic hydrocarbons, esters, ketones, glycol ethers, chlorinated solvents, drying oils, and terpenes. They are insoluble in alcohols. They exhibit wide compatibility with non-film-forming resins, waxes, plasticizers, and film-forming resins. Some of the film-forming resins with which they are compatible are butyl methacrylate, ethylcellulose, nitrocellulose, rubber, rubber hydrochloride, cyclized rubber, polyvinyl butyral, and polybutene. Some of the non-film-forming resins with which they are compatible are dammar, ester gum, rosin, manila, polystyrene, shellac, and urea-formaldehyde resins. In addition, they are compatible with asphalt, beeswax, carnauba wax, ceresin, opalwax, ozokerite, and paraffin. Some of the plasticizers which can be used with these resins are blown castor oil, butyl stearate, dibutyl phthalate, mineral oil, tricresyl phosphate, and vegetable drying oils. The resins are used in lacquer, hot melt, and latex form. Their greatest use is in adhesives where their inherent tackiness is of great value. They are also used as plasticizers and modifiers for other resins.

The methyl ester of rosin (Abalyn resin) and the hydrogenated methyl ester of rosin (Hercolyn resin) are important commercial liquid esters of rosin. These resins are miscible with ethers, organic esters, ketones, alcohols, and aromatic and aliphatic hydrocarbons. They are compatible with

[1] "Synthetic Resins," Hercules Powder Company, Wilmington, Delaware

[2] "Hercules Synthetic Resin Solutions," Hercules Powder Co., Wilmington, Delaware

[3] "Staybelite Esters," Hercules Powder Co., Wilmington, Del. (1947)

and act as solvents for many film-forming resins such as nitrocellulose, ethylcellulose, chlorinated rubber, polychloroprene, vinyl acetate-chloride copolymer, and natural rubber, but are incompatible with cellulose acetate and vinyl acetate. Some of the non-film-forming resins with which they are compatible are the alkyds, coumarone-indenes, ester gum, rosin, and urea-formaldehyde resins. They act as softening agents for the natural resins such as manila, kauri, and shellac. They are compatible with vegetable waxes and asphalt, but are incompatible with paraffin when used in minor proportions. They are sometimes used in combination with starch, casein, and animal glue to increase the toughness and flexibility of the film.

Another important group of rosin derivatives are the rosin-derived alkyd type resins (Neolyn resins). These are amber-colored resins which range from soft, balsamic materials to solid products having a softening range around 75° C. These resins are soluble in toluene, ethyl acetate, acetone, carbon tetrachloride, and chlorinated solvents, but are insoluble in aliphatic hydrocarbons, fats, oils, and waxes. They are soluble in alcohol at high resin concentrations only. These resins are compatible with nitrocellulose, vinyl acetate-chloride copolymers, polyvinyl chloride, chlorinated rubber, methyl and ethyl methacrylates, urea-formaldehyde resin, and others. They are incompatible with waxes and have only a very limited compatibility with ethylcellulose and cellulose acetate. They are used as adhesives and as coatings, being applied as varnishes, hot melts, or emulsions.

Shellac

Shellac is a resin of insect origin. India is the main source of supply. Chemically speaking, shellac is a polyester formed by the self-esterification of a mixture of hydroxy acids. These hydroxy acids are both monobasic and dibasic, but nearly all contain more than one hydroxyl group.[4] During heat treatment of shellac, ester linkages are established between chains, resulting in the formation of a three-dimensional polymer.

Shellac is sold in a number of different grades, including hard brown or orange flakes (TN, Superfine, ASO, DC). It is sold in bleached and refined grades.

Shellac is soluble in alcohol and is used in varnishes containing an alcohol solvent. Shellac is insoluble in water, but can be dispersed in water by the use of alkalies. One type of water-fast ink is based upon shellac which has been solubilized with ammonia and borax and used with a suitable dyestuff.

Dammar Resins

Dammar resins are pale, hard resins which are obtained from the relatively fresh exudations of trees which grow almost entirely in the Netherlands East Indies and Malay States. After collection, these resins are cleaned and classified according to quality. The resin has a low acid number.

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[4] C. E. Barnes, *Ind. Eng. Chem. 30,* No. 4: 449–451 (Apr., 1938)

Dammar resins are soluble in coal tar solvents, petroleum solvents, and hydrogenated petroleum solvents. They are compatible with some waxes, ethylcellulose, and some oils. The poorer grades form solutions of higher viscosity than the better grades, probably because of the presence of impurities.

Dammar resins are thermoplastic. They show good adhesion and have high water resistance. They are used in both hot melt and lacquer coatings where moisture-proofness and heat-sealing properties are desired. They are also used for decorative coatings.

Manila Resins

The manila copals constitute another important class of natural resins. They are characterized by high acid number and pale color.

Manila resins are soluble in alcohol, but are insoluble in both aromatic and aliphatic hydrocarbons. They are compatible with ethylcellulose and some vegetable oils.

East India Resins

East India resins are commonly divided into the pale and black grades. The former have light color, whereas the latter are much darker. Both are soluble in petroleum and aromatic solvents. Films produced with East India resins have good water resistance and heat-seal properties.

The Batu resins are similar to the pale resin. They have excellent water resistance.

Congo Resins

The Congo resins are the most insoluble of all natural resins. There are no solvents for these resins in their natural state, so that the resins must first be processed thermally in order to make them soluble, after which they become compatible with a wide range of solvents and drying oils.[5] The solubility of the final product depends upon the degree of heat treatment. The treated resin is hard and dark in color and has a high acid number.

Treated Congo resins are soluble in petroleum and coal tar solvents, and are compatible with ethylcellulose and vegetable oils. In addition to the regular heat-treated product, other grades are available in which the resin has been esterified with glycerine to form Congo resin esters.

Kauri

Kauri resin has high acid number. It is soluble in alcohol, but insoluble in aromatic and aliphatic hydrocarbons. It must be heat-treated to render it compatible with oils.

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[5] C. L. Mantell and R. W. Allan, *Ind. Eng. Chem. 30,* No. 2: 262–269 (Mar., 1938)

Accroides and Elemi

There are many other natural resins, but most of these are of relatively little importance to the paper chemist. The accroides and elemi resins are others which are sometimes used. The accroides are soluble in alcohol but insoluble in aromatic hydrocarbons. They are compatible with cellulose acetate. Elemi resins are soluble in alcohols and esters, and are compatible with ethylcellulose.

Zein

Zein is a protein (prolamine) obtained from corn gluten, a by-product of the wet-milling corn industries, in which it constitutes about 70% of the total protein in the gluten. Zein is extracted from the gluten with aqueous isopropyl alcohol and sold as a fine, slightly yellow powder.

Zein is soluble in methanol, ethyl alcohol (95%), and isopropyl alcohol (91%). Some water must be present to obtain solubility in alcohols, although water-free solutions can be prepared in glycols. Zein tends to denature in alcohol solution and, in time, will set spontaneously to a gel, particularly if the water content is high. Cosolvents (e.g., aliphatic esters, chlorinated hydrocarbons, and lower ketones) can be used to prepare anhydrous systems. Diluents (e.g., aromatic and aliphatic hydrocarbons) can be used if desired. Zein is compatible with acid resins such as rosin, Manila, or shellac, and also with some of the neutral resins, e.g., ester gum. Other compatible resins include the phenolics, urea resins, and coumarone-indene resins.

Zein produces oil- and scuff-resistant coatings. It is a satisfactory substitute for shellac. The coatings have low gloss, although this can be improved by the addition of resins. Zein is used in coatings for food wrappers and cartons, and in decorative solid-color printing of magazines, cover papers, and labels. Zein is not suited for the impregnation of paper because of its high molecular weight. It will dissolve in water at a *p*H of about 11.8, and will dissolve in aqueous solutions of sodium hydroxide and sodium soaps. However, zein is ordinarily not applied in this manner.

Cellulose Derivatives (Film-Forming Resins)

There are two broad classes of synthetic (and semi-synthetic) resins which belong to the film-forming group. These are the cellulose derivatives and the vinyl polymers. Some of the most important cellulose derivatives of solvent-soluble grade are discussed below.

Nitrocellulose

Nitrocellulose is the oldest cellulose ester and is still widely used because of the toughness and flexibility of its film, its relative cheapness, its compatibility with a large number of plasticizers, and its solubility in a great many solvents. Nitrocellulose is made by treating pure cellulose with a mixture of nitric and sulfuric acids until between 11.2 and 12.4% nitrogen is added in the form of nitrate, corresponding to a mixture of the di- and trinitrates. The following percentages of nitrogen correspond to the theoretical derivatives.

Trinitrate	14.16% nitrogen
Dinitrate	11.13% nitrogen
Mononitrate	6.77% nitrogen

The degree of nitration is the important factor governing the solubility of the final product. The commercial products used for lacquers are nitrated to the point where they are soluble in alcohol, acetone, or ethyl acetate. In general, nitrates of low substitution are soluble in alcohol, whereas nitrates of higher nitrogen content are soluble in acetone. The higher the degree of substitution, the lower the water sensitivity. There are two principal types, the RS (regular soluble) type, which is soluble in esters and ketones, and the SS type, which is soluble in alcohol (see Ch. XXII).

Nitrocellulose is classified according to its viscosity in standard solvent mixture, using the falling ball viscosity method. Commercial products have viscosities ranging from ¼ second to 1,000 seconds and above by this method. The viscosity depends almost entirely upon the average molecular chain length, and hence is determined by the type of cellulose used in the preparation of the derivative. As with all film-forming resins, the viscosity is an indication of the film strength. The viscosity also controls the total solids at which the resin can be applied in solvents.

Nitrocellulose is compatible with the natural resins, modified alkyd resins, rosin derivatives, polyester resins, paraffin wax, and other synthetic resins. Plasticizers such as dibutyl phthalate and tricresyl phosphate are generally used.

Cellulose Acetate

Cellulose acetate is made by heating cellulose under pressure with a mixture of acetic anhydride and glacial acetic acid, and a small amount of a catalyst such as sulfuric acid, phosphoric acid, chloroacetic acid, or zinc chloride. During acetylation, the sulfuric acid combines with the cellulose to produce a cellulose acetate acid sulfate, and it is only toward the completion of the reaction that the sulfate is gradually replaced by acetyl.[6] The reaction produces an ester with a high degree of substitution, so that it is necessary to dilute the reaction mixture with dilute acetic acid in order to hydrolyze the product to one of lower substitution. When the product

[6] C. J. Malm, L. J. Taughe and B. C. Laird, *Ind. Eng. Chem. 38*, No. 1: 77–82 (Jan., 1946)

reaches the desired degree of substitution, it is precipitated by the addition of water, after which the product is neutralized and washed.

Cellulose triacetate produces weak films, but products of lower acetyl content produce very strong films. Commercial products have an acetyl content ranging from 38.0 to 41.5%, corresponding to a mixture of the di- and triacetates. The following shows the acetyl contents for the theoretical esters.

Triacetate	44.8% acetyl
Diacetate	35.0% acetyl
Monoacetate	21.1% acetyl

The commercial acetate has a softening range of 435 to 480° F.

Cellulose acetate has lower solubility in solvents and is less compatible with resins and plasticizers than nitrocellulose. On the other hand, cellulose acetate produces films which are less flammable, more heat- and light-stable, and more solvent-resistant than nitrocellulose. The solubility depends on the degree of substitution as indicated by the acetyl content. The triacetate is not soluble in acetone, but is soluble in the less polar solvents, such as chloroform, nitrobenzene, nitromethane, and pyridine. Esters in the commercial range are soluble in acetone and methyl ethyl ketone. Co-solvents such alcohol and diluents such as toluene are sometimes added. Among the resins with which cellulose acetate is compatible are the phenolics, alkyds, and some of the natural resins. Many different plasticizers can be used.

Other Cellulose Esters

It is possible to prepare a large number of cellulose esters containing fatty acid radicals of different lengths. As the length of the substituted group is increased, the derivative becomes more soluble in non-polar solvents. Thus, cellulose tripropionate is soluble in benzene, whereas cellulose triacetate is not. Other manifestations of increased size of the substituted groups are reduced tensile strength, increased flexibility, increased softness, lower water sensitivity, and lower melting point. The densities of cellulose esters range from 1.28 for the triacetate to 1.16 for the tributyrate, compared with 1.52 for regenerated cellulose.[7]

Mixed cellulose esters can be prepared by using mixed esterifying agents. Certain mixed esters have improved properties over the pure derivatives, for example, cellulose acetate butyrate and cellulose acetate propionate have higher water resistance, more flexibility, and better compatibility with resins than cellulose acetate. The softening points are lower (e.g., 400 to 435° F. for cellulose acetobutyrate) than that of cellulose acetate (435 to 480° F.) Because of the lower softening point, cellulose acetobutyrate is more suitable for hot-melt application than cellulose acetate. The mixed esters are not used to any extent in paper coating, however, because of their higher cost.

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[7] C. J. Malm, L. B. Genung and J. V. Fleckenstein, *Ind. Eng. Chem. 39,* No. 11: 1488–1503 (Nov., 1947)

Ethylcellulose

The most important cellulose ether, from the standpoint of the coating chemist, is ethylcellulose. Ethylcellulose is sold as white, porous granules which can be used in hot-melt or solvent form to produce odorless, colorless, and tasteless coatings. The films are tough and flexible and have good heat-seal properties. Ethylcellulose is better suited for hot melts than cellulose acetate or nitrocellulose because of its better heat stability and better compatibility with film-modifying agents.[8]

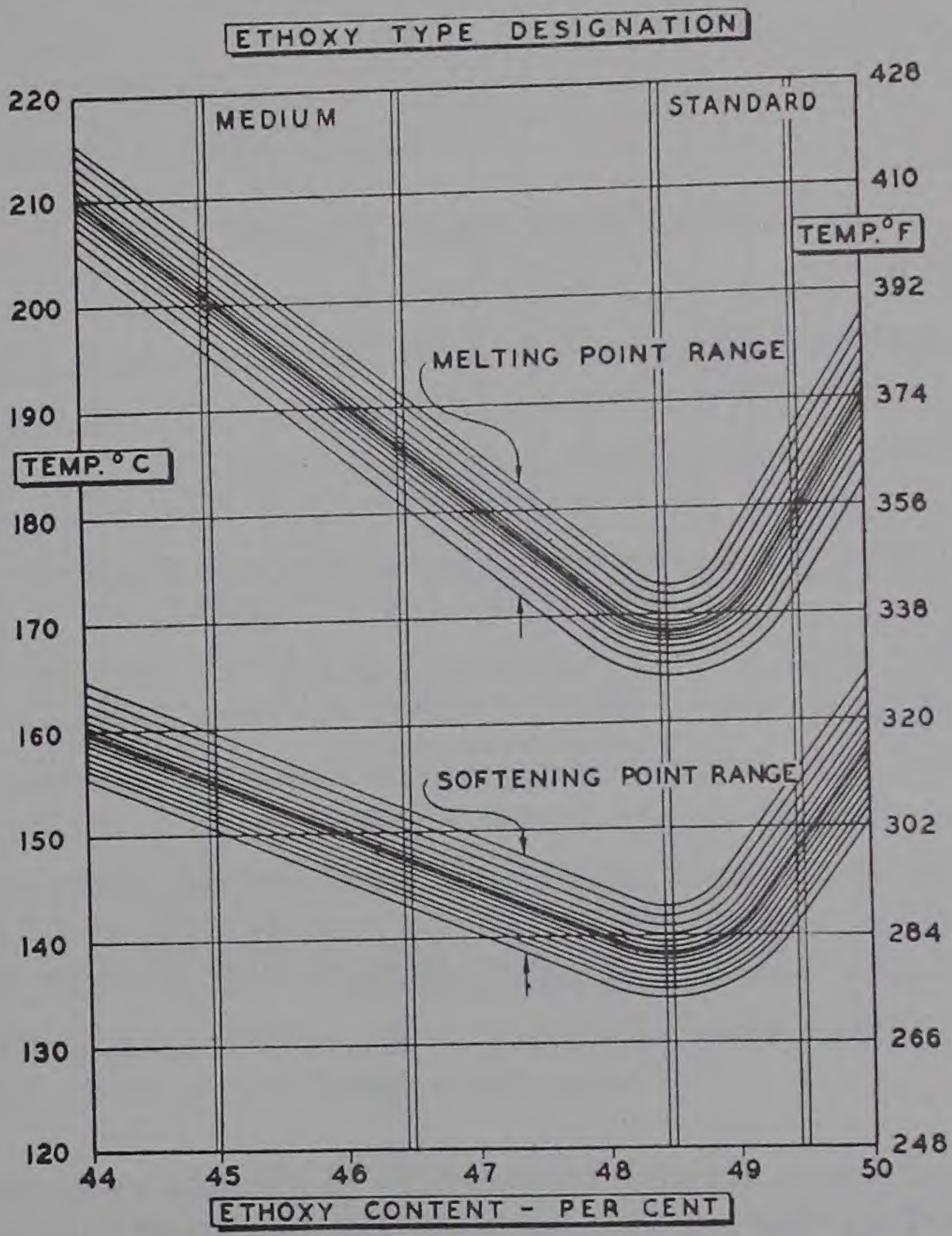

Fig. XXIII-2. Effect of ethoxyl content on the softening and melting points of ethylcellulose.

The commercial grades of ethylcellulose used in lacquers and hot-melt coatings have a degree of substitution in the neighborhood of 2.25 to 2.60 ethoxyl groups per glucose unit (46.8 to 48.5% ethoxyl content). At about this degree of substitution, ethylcellulose has its maximum solubility in mixtures of alcohols and hydrocarbons (see Ch. I). Products in this range have low softening points and the films remain flexible at low temperatures. The effect of ethoxyl content on the softening and melting points is shown in Figure XXIII-2.[9] The low ethoxyl types are not widely used because of their low solubility and reduced compatibility with resins and plasticizers.

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[8] J. H. Long, *Paper Trade J. 109,* No. 2: 38–40 (July 13, 1939)

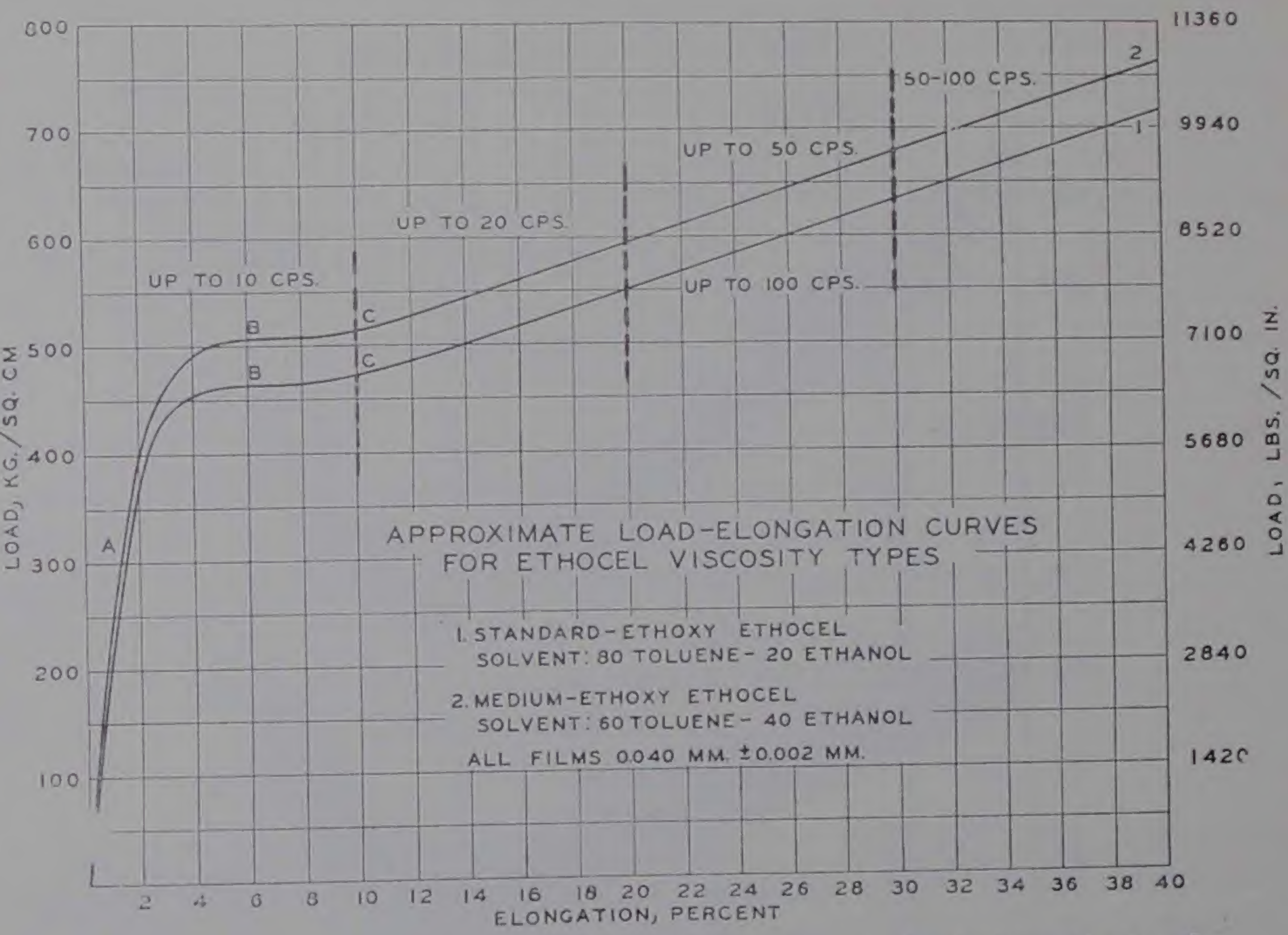

Fig. XXIII-3. Effect of viscosity on toughness (load-elongation) of ethylcellulose films.

Ethylcellulose is available commercially in different viscosities ranging from about 7 to 165 cps., measured on the Brookfield viscometer in a toluene-ethanol solvent. The viscosity influences the strength and toughness of the film, as shown in Figure XXIII-3.[9]

Resins are sometimes added to ethylcellulose to improve the gloss, adhesion, solvent resistance, and rubbing properties of the film. Ethylcellulose is compatible with the phenolics, nitrocellulose, rosin, coumarone-indenes, natural resins and long-oil alkyds, but is incompatible with the short oil alkyds and the vinyl polymers. In formulating ethylcellulose lacquers, it is not uncommon to use as much resin as ethylcellulose. The tolerance of ethylcellulose for many resins with which it is normally incompatible can be improved by incorporating a third ingredient which is a good mutual solvent, such as a fatty acid of a drying oil or rosin.[10] Ethylcellulose is compatible with montan and beeswax, but not with paraffin, unless a third ingredient (e.g., hydrogenated vegetable oil) is present. If used as a hot melt, acid resins should not be added, since they cause deterioration.

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[9] Courtesy Dow Chemical Company, Midland, Michigan (1947)

Ethylcellulose is easily plasticized with the common plasticizers, and normally, from 15 to 30% plasticizer is used. The plasticizers most commonly used are the phthalates, phosphates, stearates, castor oil, and the chlorinated biphenyls. Esters such as dioctyl phthalate and butyl stearate are best for low temperature plasticizing. Methyl phenol is said to improve the heat and light stability.

Vinyl Polymers (Film-Forming Resins)

The vinyl polymers are very important to the paper chemist because of their ability to produce tough, adhesive films which have high gloss and good heat-seal properties. There are a large number of vinyl polymers, and the field is growing rapidly. Most of these resins are suitable for lacquer and hot melts and, in addition, certain of the vinyl resins are available commercially in emulsion form. The water-soluble polyvinyl alcohol is discussed in the Chapters XI and XVIII.

Vinyl polymers are obtained through resinification of materials containing the vinyl group ($CH_2{=}CH{-}$). Polymerization of vinyl compounds is entirely different from that which occurs with phenolic, alkyd, or urea-formaldehyde resins, since it involves the self-addition of unsaturated hydrocarbon derivatives, whereas these other resins involve a condensation reaction. Polymerization of most vinyl compounds results in the formation of straight-chain products which have none of the cross linkages found in the non-film-forming resins. However, both thermoplastic and thermosetting vinyl resins are available.

Polyvinyl Acetate

Polyvinyl acetate is an important member of the vinyl polymers. It can be prepared by passing acetylene through acetic acid in the presence of the proper catalysts. The polymerization of the acetate to high molecular weight polymers proceeds rapidly in the presence of the correct catalyst and proper temperature.

Polyvinyl acetate is a thermoplastic colorless, non-toxic, odorless resin which is sold in either powder or solution form. The commercial resins vary in molecular weight, most products having a degree of polymerization of 60 to 230, although products of much higher D.P. are possible. Solution viscosity, film strength, toughness, and softening temperature all increase with increasing molecular weight.

[10] W. Koch, *Ind. Eng. Chem. 29,* No. 6: 687–690 (July, 1937)

Polyvinyl acetate has excellent solubility characteristics and is soluble in esters, alcohols (containing a small amount of water), ketones (e.g., methyl ethyl ketone), ethers, aromatic hydrocarbons, nitroparaffins, and chlorinated hydrocarbons. Ketones and hydrocarbons make the best solvents. Diluents such as xylene may be used in some formulations.

Polyvinyl acetate is compatible with a wide variety of resins, including rosin, dammar, phenolic resins, chlorinated rubber, alkyd resins, and nitrocellulose. Polyvinyl acetate can be used with a number of plasticizers.

Polyvinyl acetate is stable to heat and light and is resistant to weak acids, alkalies, and salt solutions, but is hydrolyzed by strong acids and alkalies. It has a low degree of solvent resistance and is swelled and softened upon long exposure to water. The film is softened upon exposure to temperatures above 150° F. and exhibits cold flow at even low temperatures.

Polyvinyl acetate is used in solvent coatings, particularly if good heat-sealing properties are desired. Hot-melt applications are sometimes used. Polyvinyl acetate is also available in emulsion form containing up to 60 to 65% solids. An excellent bond can be produced with these emulsions by evaporating the water in the film and curing under heat. The emulsions are often used as laminating adhesives, sometimes in combination with starch, casein, or rubber latex. Modified vinyl acetate resins containing varying percentages of hydroxyl groups are sold in solution form and are used principally as adhesives.[11]

Polyvinyl Chloride

Vinyl chloride can be prepared by passing hydrochloric acid through acetylene in the presence of a catalyst. The vinyl chloride produced in this way can be polymerized to products having a wide range of molecular weight.

Polyvinyl chloride is not so useful to the paper converter as polyvinyl acetate because of its lack of solubility in the common solvents. It is, however, soluble in some of the chlorinated hydrocarbons. Polyvinyl chloride films have a high degree of solvent resistance.

Polyvinyl chloride polymers are available as latices in three different forms (Geon resins): (*1*) unplasticized form, (*2*) externally plasticized form, and (*3*) plasticized during manufacture with nitrile type rubber. The last grade has the advantage that the plasticizer is non-volatile and non-migratory, since it is part of the resin. The unplasticized resin can be plasticized with about 35% of dioctyl phthalate. Films of the plasticized resin will fuse at about 250° F., compared with about 300° F. for the unplasticized resin.

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[11] Sold under the trade name Vinylseal by Bakelite Corp., Carbide and Carbon Chemical Corp., New York, N. Y.

Polyvinyl Chloride-Acetate Copolymers

Vinyl chloride (a gas) and vinyl acetate (a low-boiling liquid) can be copolymerized to produce vinyl chloride-acetate copolymer. Polymerization can be carried out simultaneously in the presence of acetone and the polymer precipitated in the form of a powder by the addition of water. Resins formed in this manner combine the high chemical resistance, water resistance, and toughness of polyvinyl chloride, and the excellent solubility and softness characteristics of polyvinyl acetate. The proportions of the two monomers can be varied to secure the desired combination of properties. One of the first copolymers made contained 87% vinyl chloride and 13% vinyl acetate. Today, copolymers ranging from 3% vinyl acetate and 97% vinyl chloride to 38% vinyl acetate and 62% vinyl chloride are available. The copolymers are available in different viscosities. They are widely used in lacquer coatings (see Ch. XXII).

Polyvinyl chloride-acetate copolymers are soluble in ketones, cyclic ketones, esters, chlorinated hydrocarbons, nitroparaffin, *n*-butyl acetate, dioxane, and certain chlorinated hydrocarbons. Methyl ethyl ketone, nitromethane, and mesityl oxide are some of the solvents which have been used commercially. The resin is insoluble in aliphatic hydrocarbons. The resin is swelled by aromatic hydrocarbons and some grades are soluble in aromatic hydrocarbons (e.g., toluene and xylene), particularly at high temperatures. Toluene is often used as a diluent for part of the ketone solvent. Copolymers containing high percentages of vinyl chloride (over 90%) require strong solvents, such as methyl ethyl ketone, cyclohexanone, or mesityl oxide. If these grades are used as lacquers, a high ratio of plasticizer of the solvent type must be used. Tricresyl phosphate, butoxyglycol phthalate, and ethyl hexyl phthalate are some of the suitable plasticizers.

Polyvinyl chloride-acetate copolymers are sometimes used as organosols. In this way, high-solids coatings can be applied in the presence of low-cost thinners and dispersants. These resins are also available in emulsion form. These emulsions are used as laminating adhesives, particularly for metal foils, and for treating paper to improve the water and grease resistance.

Polyvinyl chloride-acetate copolymers are compatible with rosin, certain of the phenolic resins, chlorinated diphenyls, alkyds, coumarone-indenes, chloroparaffins, methacrylates, ester gum, accroides, elemi gum, and other vinyl resins. They are not compatible with drying oils, non-drying oils, certain of the phenolics, and certain of the natural resins.

Several modifications of polyvinyl chloride-acetate copolymers have appeared in recent years. One of these is actually a tripolymer in which a small quantity of unsaturated dibasic acid is reacted chemically with the monomers during polymerization. Another modification consists of removing part of the acetate and chloride groups from the copolymer and replacing with hydroxyls.[12] Better compatibility with alkyl resins, oleoresinous varnishes, and waxes is claimed.[13]

Polyvinylidene Chloride and Copolymers

Polyvinylidene chloride copolymers are vinyl type resins, although their properties are quite different from other vinyl resins. Copolymers of polyvinylidene chloride-acrylonitrile are sold commercially under the trade name of Saran.[14]

Polyvinylidene chloride copolymers are soluble in mesityl oxide, cyclohexanone, and methyl ethyl ketone, the latter being the most widely used. Diluents can be used (see Ch. XXII).

Polyvinylidene copolymer is compatible with the phenolics, polystyrenes, certain of the acrylates, ester gums, chlorinated paraffins, and other vinyl resins. A small percentage (1–15%) of solvent type plasticizer may be used. Plasticizers lower the water-vapor resistance, but may be desirable when low-temperature flexibility is desired. There are only a relatively few plasticizers which produce clear films with a high degree of flexibility. Phthalates improve the adhesion to metal foils.

Polyvinylidene copolymer resins are available in latex form. The commercial latex consists of a colloidal dispersion of about 60% solids containing dispersed particles ranging from 0.008 to 0.15 micron in size. The viscosity is about 22 cps. at 57% solids. The *p*H of the latex is close to the neutral point, but the stability is relatively unaffected by changes in *p*H from 2 to 12.[15] The latex is coagulated by electrolytes in fairly low concentrations, although ordinary hard water has relatively little effect. Additional plasticizer is sometimes required with the commercial latex. The most effective plasticizers are the organic esters of phthalic, glycolic, sebacic, and phosphoric acids.

Polyvinyl Aldehydes

A large number of polyvinyl aldehydes are of interest to the paper coater. These are prepared by hydrolyzing polyvinyl acetate to polyvinyl alcohol and then reacting the alcohol with a suitable aldehyde. The final product usually contains some free hydroxyl groups which account for the high water absorption of this resin. Among the commercial products are

[12] Vinylite VAGH, Bakelite Corp., Carbide and Carbon Chemical Corp., New York, N. Y.

[13] C. W. Patton, *Official Digest*, New York Paint and Varnish Production (May, 1948)

[14] Dow Chemical Co., Midland, Michigan

[15] G. W. Stanton and W. A. Henson, *Paper Trade J. 123*, No. 6: 68-72 (Aug. 8, 1946)

polyvinyl formal, polyvinyl acetate, and polyvinyl butyral. The simpler aldehydes yield harder, less soluble resins than the higher aldehydes.

Polyvinyl butyral has shown the most promise of the resins in this group. It is soluble in esters and alcohols and is compatible with a number of natural and synthetic resins. It is suitable for use in lacquers or in hot melts, and is also available in emulsion form. Films formed from polyvinyl butyral are tough, flexible, and resistant to gases, but are not very resistant to water, acids, and alkalies.

Polystyrene

Styrene is a clear colorless liquid which contains a benzene nucleus and a vinyl grouping. Polystyrene, which is one of the oldest synthetic resins, is formed by the polymerization of styrene. The resin is brittle and low in strength, but has a high degree of chemical resistance, good electrical properties, and good water resistance. Dichlorostyrene has better heat and chemical resistance than polystyrene. Various copolymers of styrene with other resins show good all-round properties.

Polystyrene resins are available in a wide range of melting points, viscosities, hardness, and solubility. These range from low-melting, friable products to high-melting, tough products, with molecular weights ranging from 6,000 to about 85,000. They are used in lacquer and hot melts and are also available in emulsion form. Polystyrene resins are soluble in esters, ketones, aromatic hydrocarbons (xylene and toluene), high-solvency aliphatic hydrocarbons, and chlorinated hydrocarbons. In the low-viscosity grades, the toluene solution can be diluted with large volumes of cheap aliphatic hydrocarbons such as troluoil. Solvent coatings brush well and release the solvent readily.

Polystyrene résins are compatible with the phenols, melamine resins, coumarone-indenes, and toluene-sulfonamides, but are incompatible with the alkyds, vinyls, acrylates, cellulose derivatives, and polybutene resins. They are compatible with the common plasticizers such as the phosphates, phthalates, sebacates, and abietates. In general, however, plasticizers are not very useful, since low concentrations result in films which are brittle, whereas high concentrations result in films which are very soft and tacky. The commercial products are sometimes modified with plasticizers added by the supplier. Internal plasticization of styrene results in permanent changes in flexibility and there is one product (Dow 512-K) which is very useful in paper coating. Straight styrene latices are available (Lustrex).

Acrylic and Methacrylic Polymers

Acrylate and methacrylate resins are made by the polymerization of esters of acrylic and methacrylic acids, respectively. Acrylic acid can be produced by a series of reactions whereby ethylene and hypochlorous acid are reacted to produce ethylene chlorohydrin, which reacts with sodium cyanide to form ethylene cyanohydrin. Upon the elimination of water, acrylic nitrile is formed, which in turn can be readily hydrolyzed to acrylic acid. This acid may be reacted with alcohols directly to form the ester, or ethylene cyanohydrin may be used. Esters of methacrylic acid may be obtained by reaction of the ketone cyanohydrin with the alcohol, e.g., by reaction of methyl alcohol and acetone cyanohydrin.

The resins are sold as water solutions of the polyacrylic salts, as solvent-soluble resins, or as emulsions. According to Staudinger,[16] ethyl acrylate polymers vary from viscous colorless oils at a molecular weight of 2,200, to tough, somewhat fluid substances at a molecular weight of 7,800, and to tough elastic solids at a molecular weight of 175,000. The properties of the resin depend upon the properties of the alcohol used in making the ester; for example, polymethyl acrylate is tough, pliable and elastic, polyethyl acrylate is softer and more elastic, and polybutyl acrylate is very soft and almost sticky at the same degree of polymerization.

Commercial acrylate and methacrylate resins are suitable for use in hot melts, saturants, and lacquers. The films are soft and somewhat tacky, and hence the resins are useful in pressure-sensitive adhesives. The resins are soluble in esters, ketones, chlorinated hydrocarbons, furfural, dioxane, and other solvents. They are compatible with a large number of resins, including the cellulose derivatives.

Acrylic resin is available in emulsion form suitable for use as adhesives and for coating and saturating. It produces very clear films ranging from hard and brittle to soft and flexible. Recently non-ionic grades have been produced which have high mechanical stability, a high tolerance for inorganic salts, and good stability at low *p*H values.

Polyethylene Resins

Polyethylene resins are one of the newer resins, having been made commercially in the United States only since 1942. Polyethylene resins are obtained from the polymerization of ethylene at high pressures and temperatures. The resins are essentially linear polymers of ethylene ranging in molecular weight from 1,000 to 40,000.[17] The commercial coating resins have molecular weights in the range of 12,000 to 19,000 and are wax-like substances resembling paraffin. The resins are crystalline and have rather sharp melting points, usually around 102 to 110° C.

Polyethylene resins have excellent chemical resistance, excellent water resistance, high water-vapor resistance (but low resistance to most other gases), and very good electrical properties. The resins are odorless, tasteless, non-toxic, and have a low specific gravity. They have good heat sealability and are very flexible even at low temperatures. Their low dielectric loss makes them valuable as electrical insulators in high-frequency equipment. Polyethylene coatings are used on paper bags for the packaging of food products and hygroscopic materials and for wrappers for frozen foods. The coating is generally done by the extrusion process.

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[16] H. Staudinger and E. Trommsdorf, *Ann.* 502, 207 (1933) from *C. A. 27:* 4213 (1933)

[17] J. K. Honish, *Paper Trade J. 128,* No. 15: 125–127 (Apr. 14, 1949)

Polyethylene resins are insoluble in all organic solvents at room temperature, but they begin to dissolve in a number of solvents at temperatures of 50 to 60° C. (see Ch. XXII). The resins are used in lacquers or in hot melts, generally mixed with paraffin. They are available commercially as water dispersions. These resins are compatible with coumarone-indene resins, some of the synthetic rubbers, ester gum, chloroparaffins, ethylcellulose, phenolic resins, and paraffin. Plasticizers are rarely needed with the polyethylene resins because of their inherent flexibility.

Synthetic Non-Film-Forming Resins

The synthetic resins in the non-film-forming group represent a large and important group of industrial resins. These are made from industrial chemicals which are built up into resinous compounds by polymerization or condensation. Polymerization can produce linear molecules or it can produce branched molecules, depending upon the type of monomer and the conditions under which polymerization is carried out. Even a small amount of cross linking (often less than 1%) results in a very marked decrease in the solubility of the resin.

Polymerized resins are characterized as either (*1*) thermoplastic resins, which soften on heating, but can be resolidified and resoftened indefinitely, or (*2*) thermosetting resins, which are changed on heating into insoluble, infusible products. Film-forming resins are generally thermoplastic. Non-film-forming resins are generally thermosetting, although there are many members of this group which are thermoplastic. Thermosetting resins are often sold in the partially polymerized state so that the final polymerization can take place after the resin has been applied. Three stages are recognized in the polymerization of thermosetting resins: A-stage, where the produce is soluble and fusible; B-stage, where the product is less soluble and difficult to fuse; C-stage, where the produce is insoluble and infusible.

Mark[18] lists the important characteristics of high polymers as follows: (*1*) average molecular weight, (*2*) chain length distribution, (*3*) chemical nature, and (*4*) intermolecular forces between molecules. The solubility characteristics depend upon the size and shape of the molecule and upon the degree of branching. Linear resins tend to be soluble in all stages, whereas the cyclic resins form insoluble products in the higher stages of polymerization.[19] Linear molecules tend to associate with one another, but this cohesion is broken by solvents, which force themselves between the linear chains. Cyclic chain molecules, on the other hand, are bound together by primary valence forces which cannot be ruptured by solvents. In highly concentrated solutions, linear molecules may orient themselves to form micelles leading, in extreme cases, to gel formation.

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[18] H. Mark, *Ind. Eng. Chem. 34,* No. 11: 1343–1348 (Nov., 1942)

Phenol-Formaldehyde Resins

Phenol-formaldehyde resins are prepared by the interaction and polymerization of phenol and formaldehyde. They were among the earliest of the synthetic resins, having been actively investigated by Baekland in 1905 to 1907. Phenolic resins have good heat and chemical resistance and good electrical properties, but the color is poor.

The properties of phenolic resins can be regulated by varying (*1*) the type of phenolic body used (e.g., phenol, cresol, xylenol, or resorcinol), (*2*) the type and amount of catalyst, and (*3*) the ratio of reactants. By changing any of these factors, it is possible to obtain a slow- to fast-setting resin, a resin with poor to good dielectric properties, a resin with poor to good alkali resistance, etc. For example, straight phenol-formaldehyde produces a resin with the highest mechanical strength, whereas cresol-formaldehyde produces a resin with the best electrical properties. Resorcinol reacts more readily with formaldehyde than phenol and produces products which are noted for their good adhesive qualities. Resorcinol-formaldehyde resins are particularly well suited for low-pressure laminating. Other aldehydes, aside from formaldehyde, may be used in special cases (e.g., furfuraldehyde).

Phenolic resins may belong to the thermosetting class (Bakelite resins) or to the thermoplastic class (Novolak resins). The fusible types appear to possess a linear structure, whereas non-fusible types appear to have a cyclic structure.[20] Linear molecules are produced in the early stages of polymerization, but these are changed to a complex cyclic structure by the formation of comparatively few cross linkages. The chains contain phenol molecules attached to one another by CH_2 groups.

In general, high temperatures and either highly acid or highly alkaline conditions are required in the final curing (polymerization) of phenolic resins. The *p*H at which polymerization is carried out is a factor determining the properties of the resin. Resinification under acid conditions leads to the formation of resins containing the diphenyl methane group. Alkaline-catalyzed resins contain a higher percentage of formaldehyde than

[19] W. B. Reynolds, *Chem. Eng. News 24*, No. 7: 916–918 (Apr. 10, 1946)

[20] J. B. Niederl and J. S. McCoy, *J. Am. Chem. Soc. 65*, No. 4: 629–631 (Apr., 1943)

acid-catalyzed resins. They contain methylol groups (CH_2OH) in the chain.[21]

Phenol-formaldehyde resins are made in both the water-soluble (approximate molecular weight 150 to 200) and alcohol-soluble grades (approximate molecular weight 200 to 500). Water-soluble but acid-precipitable grades are also produced. Both the water- and alcohol-soluble grades are used in making paper laminates. Around 1910 to 1920, a new series of phenolic resins was developed which were soluble in oleoresinous varnishes. These resins provided the first competition to the natural resins, and since then, have replaced the natural resins for protective coatings and plastics. These resins are made by reacting alkylated or arylated phenols with rosin or similar materials. These resins are soluble in esters and aromatic solvents, and some are soluble in alcohols. Both reactive and nonreactive types are sold, the latter undergoing further condensation when cooked with drying oils in the varnish kettle.

Urea-Formaldehyde Resins

Urea-formaldehyde resins are produced by the condensation of urea and formaldehyde under controlled conditions of temperature, *p*H, and concentration. The reaction can be controlled to produce (*1*) dry crystalline water-soluble products, (*2*) aqueous syrups, or (*3*) products soluble in organic solvents. These resins are relatively new, having been produced on a large scale only since 1930. The resins are inferior to the phenolic resins in chemical and electrical resistance, but have better color.

Monomethylol and dimethylol urea are the first products formed in the reaction, being formed by the condensation of one and two formaldehyde molecules, respectively, with each urea molecule. Dimethylolurea, which contains two hydroxyl groups, can react further by (*1*) condensing to produce methylene urea, (*2*) by reacting with another urea molecule, or (*3*) by reacting with an amine group of a molecule of monomethylol urea. The reactions become very complex and result in the formation of long-chain linear molecules or in the building up of branched molecules by cross linkage, depending upon the conditions under which the reaction is carried out. Ratios of formaldehyde to urea of greater than 1 to 1 are necessary to permit the formation of three-dimensional structures.[22] Too high a ratio of formaldehyde to urea results in a molecule which is difficult to polymerize.

During polymerization, the molecular weight increases, and the viscosity of the medium increases. In the early stages, the resin is soluble in water, but if the reaction is carried far enough, the resin becomes insoluble in water. The resin passes through several stages, which Auten[23] classifies as follows:

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[21] H. Kline, *Paper Trade J. 119*, No. 13: 128–130 (Sept. 28, 1944)

[22] T. S. Hodgins and A. G. Hovey, *Ind. Eng. Chem. 31*, No. 6: 673–678 (June, 1939)

A-stage methylol derivatives, analogous to monomers.

B-stage linear molecules in intermediate stage of polycondensation. Resins are soluble or dispersible in water.

C-stage insoluble, infusible, hard stage with molecules in two- or three-dimensional network.

In the B-stage, the resins have definite colloidal properties and behave as protective colloids. They precipitate from solution upon dilution with large quantities of water. In this stage, the resins are very reactive and cannot be stored more than a few months. Both the A-stage and B-stage low molecular weight polymers will react with cellulose.

A-stage resins are sold as aqueous solutions or as spray-dried powders which are readily dispersible in water. These can be further polymerized during use by reacting under acid conditions, high temperature (250° F.), or a combination of both. Alum and ammonium salts of strong acids (e.g., ammonium chloride) are catalysts commonly used to increase the rate of polymerization.

Within recent years, a new type of water-soluble modified urea-formaldehyde resin has been developed in which the conventional resin is modified by introducing electrolytic groups at intervals along the chain. This increases the size of the molecule, but maintains the water solubility. One type is modified with sodium-sulfonate to produce a resin which is anionic in character and is precipitable with cations.[24] Another type is cationic in nature. These resins are used in making wet-strength papers (see Ch. XII).

Urea resins condensed in aqueous media are not compatible with non-aqueous solvents. However, if the reaction is carried out in the presence of monohydric or polyhydric alcohols, the alcohol takes part in the reaction, forming products of unusual solubility characteristics. In this way, etherification takes place, resulting in the introduction of alkoxyl groups.[25] Examples are the butylated and isobutylated ureas which are prepared in butanol and isobutanol, respectively. The modified resins are soluble in nearly all common organic solvents, including the aromatic hydrocarbons and mixtures of alcohol and petroleum solvents. Furthermore, the resins are compatible with a wide variety of other resins. These modified resins can be used in varnishes. If desired, the resin can be modified in the presence of the ingredients of an alkyd resin to form a complex mixed condensate containing up to 80% alkyd resin. This results in a highly flexible product.

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[23] R. W. Auten, *Paper Trade J. 127*, No. 5: 332–338 (July 29, 1948)

[24] R. W. Auten and J. L. Rainey, U. S. 2,407,599 (Sept. 10, 1946)

[25] T. S. Hodgins, A. G. Hovey, S. Hewitt, W. P. Barrett and C. J. Meeske, *Ind. Eng. Chem. 33*, No. 6: 769–779 (June, 1941)

Melamine-Formaldehyde Resins

Melamine-formaldehyde resins are similar to urea resins in general properties and behavior. They are newer than the urea resins, having been produced in the United States in quantity only since 1939. Melamine resins have greater heat and light stability, and greater moisture and chemical resistance than urea resins, but are considerably more expensive.

Melamine differs from urea in being more resistant to hydrolysis and more resistant to heat, and these characteristics are carried over into the respective resins. Melamine contains six amino groups (in comparison with two for urea), which means that it can react with as many as six formaldehyde molecules to form hexamethylol melamine. Resins can be formed from this monomer by esterification, by condensation (through elimination of water and formation of ether linkages), or through the formation of methylene linkages.

Water-soluble melamine resins are used in the preparation of wet-strength papers. In this process, the resin is condensed into a positively charged (cationic) colloid which can be added directly to the pulp to produce a high degree of wet strength.[26] (See Ch. XII.)

Solvent-soluble grades of melamine resin are produced by the introduction of alkoxyl groups in the same manner as previously discussed for urea resins. The modified melamine resins are superior to the equivalent urea resins in curing speed and chemical resistance. At normal curing temperatures of 250 to 300° F., the melamine resins require approximately one-third less curing time than the ureas.[27]

Acetone-Formaldehyde Resins

Within recent times, new water-soluble resins of the ketone-aldehyde (acetone-formaldehyde) type have been developed. These resins cure at *p*H values above 7, preferably in the range of 9.5 to 10.0, and consequently offer promise for applications where it is necessary to cure the resin under alkaline conditions. A small amount of resorcinol is said to promote the cure of these resins.

Alkyd Resins

Alkyd resins are formed by the interaction (polyester formation) of polybasic acids and polyhydric alcohols. The most common type is made from phthalic anhydride and glycerol. There are, however, a number of special types of alkyd resins. Both thermopalstic and thermosetting products can be made. For example, the reaction of glycerine and phthalic anhydride produces a thermosetting resin, whereas the reaction of a glycol and phthalic anhydride produces a thermoplastic resin. Alkyd resins may be divided into the following types: thermoplastic, thermosetting, unmodified, oil-modified, non-oxidizing, semi-oxidizing, and oxidizing. The modified grades are more important than the unmodified grades.

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[26] H. P. Wohnsiedler and W. M. Thomas, U. S. 2,345,543 (Mar. 28, 1944)

[27] R. W. Auten, *Paper Trade J. 127*, No. 5: 332–338 (July 29, 1948)

Phthalic acid reacts readily with glycerine at 200° C. Esterification takes place rapidly with the formation of acid phthalate esters. First, clear straw-colored solutions are produced, but if the heating is continued at high temperatures, an infusible, insoluble resin is formed. Commercial alkyd resins vary from liquids to hard, brittle solids, depending upon the type of acid and alcohol used and the conditions under which the reaction is carried out. They are available in both water- and solvent-soluble grades. One type is soluble in water, but precipitable by acids. As a class, they have good insulating and adhesive qualities and good grease resistance, but are low in water resistance. The important properties of alkyd resins are color, softening point, and acid number.

Modified alkyds are made by the substitution of long-chain monobasic acids or fatty-acid oils for part of the phthalic anhydride. This produces resins of reduced thermosetting properties, improved solubility in organic solvents, and increased flexibility. By varying the amount of oil or oil fatty acid, it is possible to obtain products ranging from hard brittle solids to soft plastic products. Oil-modified alkyds are classified as long or short, depending upon the relative ratio of oil or oil acid to phthalic anhydride. Long-oil alkyds dry more slowly than short-oil alkyds.

Either drying or non-drying oils (or oil acids) may be used for making oil-modified alkyds. Non-drying oils (e.g., castor oil) produce products that are compatible with nitrocellulose, urea-formaldehyde, or melamine-formaldehyde resins. These resins have good heat stability and are generally used with urea-formaldehyde or melamine-formaldehyde resins in baking finishes, principally for their plasticizing and toughening effect. Drying-oil alkyds are used in either air-drying or baking type coatings where they produce harder finishes than the non-drying oil type. Air-drying and baking alkyds may be used as the total vehicle, or they may be used in lacquer formulations. Both drying and non-drying oil-modified alkyd resins are used in nitrocellulose lacquers. Modified alkyd resins are available which are soluble in esters (ethyl and butyl acetate), ketones (acetone and methyl ethyl ketone), aromatic hydrocarbons, chlorinated hydrocarbons, hydrogenated solvents, glycol ethers and esters, and turpentine. Some grades are soluble in aliphatic hydrocarbons. The long-oil types are very compatible with raw and bodied oils.

Another type of alkyd is made by modifying with rosin or rosin derivatives. This type of modification increases the solubility in organic solvents, but produces a product of lower flexibility and reduced color compared with other alkyds. Alkyds modified with pentaerythritol have good water and chemical resistance and good curing properties.

Polyester Resins

A special type of alkyd resin, known as the polyester resin, is made by the esterification of long-chain polybasic acids (sebacic, maleic, etc.) with polyhydric alcohols, such as glycerol or ethylene glycol. These resins have exceptional toughness and flexibility and are used as plasticizers for more brittle resins, such as nitrocellulose, ethylcellulose, and polyvinyl chloride. They are made in both oil-modified and unmodified grades. The commercial products range from viscous liquids to rubbery semi-solids. They are supplied as liquids containing 100% solids or concentrated solutions in an ester solvent. The color ranges from water-white to pale yellow.

Polyester resins are sold in the partially polymerized state so that the final polymerization is carried out after application. These resins undergo molecular addition rather than condensation The addition of a small quantity of organic peroxide just prior to application transforms the resins in a short period of time into a hard, infusible plastic. The resins are used mostly for molded products where their short curing cycle has been a definite advantage. They are also used in the manufacture of paper laminates where they add chemical, heat, and oil resistance to the product and provide good electrical properties, good strength properties, and good dimensional stability. The temperature of curing generally runs from 220 to 305° F.

Other Resins

One type of ester resin which has enjoyed widespread use for many years is ester gum. This product, which is made by the reaction of rosin and glycerol, resembles shellac in its properties and has been widely used in varnishes.

An interesting new group is the maleic resins, which are made from maleic anhydride and related materials such as glycerol and pentaerythritol. These resins are characterized by high melting point, hardness, and rapid solvent release.

Another important group of resins are the polyamides made by copolymerization of long-chain organic acids with ethylenediamine. These resins are available in a wide range of properties.

One of the interesting new resins is a rosin-maleic anhydride condensation product sold under the trade name of Mersize.[28] This resin has been widely used as a partial replacement for rosin in the internal sizing of paper. Maleic rosin type phenol-formaldehyde resins have been used for paper coating. Another resin is made by the condensation of terpene polybasic acid (Petrex acid) and maleic anhydride. These resins are sold under the trade name of Petrex resins.

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[28] Monsanto Chemical Company, St. Louis, Missouri

Coumarone-Indene Resins

Coumarone-indene resins are mixtures of polymers obtained from the polymerization of the distillates from coke ovens, consisting mostly of a mixture of coumarone and indene. The distillates are polymerized either catalytically (acid conditions) or thermally to yield resins of the desired properties. The resins obtained are thermoplastic and range from viscous liquids to brittle solids. They range in color from a pale yellow to a dark brown.

Coumarone-indene resins are characterized by low acidity and a high degree of chemical resistance. They are non-saponifiable and have an acid number less than 1, which makes them useful in coatings requiring a high degree of alkali resistance. The resins have a dark color and bad odor, and these two factors have limited their use in the paper industry. They are used, however, in varnishes to extend phenolic resins, and in hot melts.

Coumarone-indene resins are compatible with a great number of resins and waxes, including the phenolics, some of the alkyds, paraffin (partly), asphalt, some of the synthetic rubbers, rubber derivatives, ethylcellulose (partly), shellac, chlorinated diphenyls, polystyrenes, rosin, and ester gum. They are not compatible with nitrocellulose and cellulose acetate.

Coumarone-indene resins are soluble in most organic solvents except the alcohols. Some of the common solvents are turpentine, esters, ethers, ketones, aliphatic hydrocarbons, aromatic hydrocarbons, and chlorinated hydrocarbons. Aromatic hydrocarbons are exceedingly strong solvents, and benzene gives the lowest viscosity solution. The resin may be dissolved cold by stirring for several hours, or the resin and solvent may be heated to a temperature not in excess of 218° C. to obtain more rapid solution. Solubility in paraffinic solvents is inversely proportional to the melting point of the resin. The stability of naphtha solutions may be improved by replacing part of the naphtha with aromatic solvent. The resins are sold commercially at 60 and 70% concentration in Hi-Flash solvent and can be thinned to normal working solids with low-solvency mineral spirits. Coumarone-indene resins are soluble in raw and heat-bodied oils (including dehydrated castor oil), but are not soluble in castor oil. Some of the modified grades are soluble in mineral oils.

Coumarone-indene resins are available in emulsion form and can be used in combination with paraffin wax emulsions, alkyd resin emulsions, and synthetic rubber emulsions. When used in combination with natural rubber latex, the *p*H should be raised to 10 to prevent coagulation of the rubber. This can be done by adding a solution of 10% sodium hydroxide.

Phenol-modified coumarone-indene resins can be prepared by polymerizing the resin in the presence of phenols or cresols. The phenol-modified resins are soluble in alcohols and show greater compatibility with a number of resins than the unmodified types. These modified resins are compatible with nitrocellulose lacquers. The alkylated phenol-modified types are soluble in practically every solvent except water and methanol. They are the most compatible of the coumarone-indene resins, being the only type compatible in all proportions with vinyl copolymers. These grades are used in ethylcellulose, nitrocellulose, and cellulose acetate lacquers. Hydrogenated coumarone-indene resins are used when improved color and odor are desired.

Terpene Resins

The terpene resins are produced by the polymerization of pinenes, both alpha- and beta-pinene being used. They are thermoplastic and are characterized by a high degree of chemical and grease resistance.

The resins are soluble in high-boiling alcohols, esters, ketones, aliphatic and aromatic hydrocarbons. They are compatible with paraffin, other waxes, rosin, asphalt, and rubber derivatives. Some of the terpene resins act as heat and light stabilizers for nitrocellulose, ethylcellulose, vinyl resins, and rubber derivatives.

Silicone Resins

The silicones contain atoms of silicon surrounded by atoms of oxygen and carbon and, as such, are both organic and inorganic in nature. The resin has a high degree of heat and chemical resistance and excellent electrical resistance. It is non-inflammable (flash point, 600° F.).

Silicone resins are soluble in toluene, ketones, and many other organic solvents. They are compatible with the cellulose derivatives, phenolics, urea resins, and some of the natural resins. They are not widely used as paper coating resins because of their high cost and because of the relatively long curing schedules and high temperature required. They have been suggested for sizing of paper, and recently, papers treated with silicone resin have been sold for use as lens cleaning tissue.

Chlorinated Polyphenyls

The chlorinated polyphenyls, sold under the trade name of Aroclors,[29] belong to the class of semi-synthetic thermoplastic resins. The commercial products range from water-white, mobile liquids and pale yellow viscous oils to sticky or hard dark brown resins, depending upon the degree of chlorination.

The resins are thermoplastic and non-drying, and the softer types have a definite plasticizing effect on other resins (e.g., nitrocellulose and ethylcellulose). They have good electrical characteristics, high dielectric strength, and low power factor. Paper for electric condensers is sometimes made by submerging the paper in a bath of chlorinated biphenyl resin. The resins are also used in coating and for laminating.

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[29] Monsanto Chemical Company, St. Louis, Missouri

These resins are soluble in most common organic solvents. They are very soluble in aliphatic hydrocarbons, aromatic hydrocarbons, and in esters. The hard crystalline resins are less soluble than the oils and soft resins. They are compatible with ethylcellulose, nitrocellulose, rubber, rubber derivatives, paraffin, coumarone-indene resins, rosin, dammar, polystyrene, styrene-butadiene copolymers, and vinyl polymers. They are incompatible with cellulose acetate.

Aryl Sulfonamide-Formaldehyde Resins

The aryl sulfonamide-formaldehyde resins are made by the condensation of formaldehyde with aromatic sulfonamides. These resins are sold under the trade name of Santolites.[30] They range from soft, yellow, sticky products to hard, water-white, brittle solids. They are highly soluble in esters, ethers, alcohols, ketones, and aromatic hydrocarbons, but are insoluble in aliphatic hydrocarbons and vegetable oils. The solvent release from high molecular weight alcohols is low. They are available commercially as solid resins, or as an 80% solution in normal butyl acetate. They are compatible with the vinyl resins, cellulose derivatives, chlorinated rubber, A-stage phenolic resins, polyvinyl chloride, polyvinyl acetate, polyvinyl copolymers, and some of the natural resins. They are not compatible with paraffin. They can be used in lacquers at high solids where they produce films having good moisture-resistance and good heat-seal properties. Their excellent compatibility with plasticizers and other resins reduces the danger of blushing and sweating in the coating.

In the same class (also known by the trade name of Santolites) are the resinous condensation products of toluene sulfonamide, formaldehyde, and alkyd resins. These range from soft, sticky resins to hard products which have the qualities of both the sulfonamide and alkyd resins. They are soluble in practically all common organic solvents except the petroleum hydrocarbons. They are compatible with cellulose ethers and cellulose esters, as well as other resins, but are not compatible with drying oils.

Rubber and Rubber Derivatives

Rubber is used in the paper industry in the form of rubber latex, which is the natural milky substance secreted by the rubber tree, or dissolved in organic solvents. Rubber latex is the more important to the paper chemist. Within recent years, synthetic rubbers and rubber derivatives have replaced the natural product for many uses.

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[30] Monsanto Chemical Company, St. Louis, Missouri

Natural Rubber Latex

Rubber latex is a milky liquid which contains extremely small, pear-shaped particles of rubber suspended in an aqueous medium. Latex has a solids content of about 35 to 40% as it comes from the tree. The latex can be used at this solids, or it can be concentrated to a solids content of 50 to 70%. Most of the latex comes from the Far East and is shipped to the United States in tankers.

The particles of dispersed rubber are non-uniform in size and vary from 0.5 to 2.0 microns on the minor axis, and from 4 to 5 microns on the major axis.[31] The particles are in the colloidal range and exhibit Brownian movement.[32] The particles consist of a tough elastic shell surrounding more distensible rubber in the center of the particle. A non-hydrocarbon serum acts as a protective colloid by surrounding the latex particles with a strongly adsorbed surface layer of protein. This serum is subject to bacterial decomposition and must be protected from spoilage. Ammonia added at the time of tapping provides sufficient preserving action.

The rubber particles in latex are relatively easily coalesced into larger particles. To prevent coalescence, the *p*H must be maintained around 11.0. If the latex is diluted, soft water should be used, because hard water tends to cause creaming, i.e., rising of rubber particles to the surface of the latex. A crude test to determine the stability of rubber latex is based upon the length of time a small sample can be rubbed between the fingers before a coagulated film is produced.[33] Casein or animal glue are sometimes added as stabilizing agents.

Other substances are frequently incorporated into crude rubber latex just before use in order to obtain the desired effects. Sulfur and accelerators are added to vulcanize the rubber, and anti-oxidants are frequently added to improve the aging properties. These materials must first be emulsified before being mixed with the latex. Rubber latex is used as a saturant in the manufacture of artificial leathers to increase the tear, fold, flexibility, and resistance to wear of the paper. It is also used as a laminating adhesive.

Natural Rubber and Rubber Derivatives

Natural rubber is dispersible in a number of different solvents. The solvent causes swelling of the rubber micelles, forming solvated units which immobilize a high percentage of solvent. The viscosity is proportional to the swelling power of the solvent,[34] and in general, the viscosity is quite high and the solution is unstable. The low solubility of natural rubber in organic solvents and the instability of rubber to high temperatures has prevented its widespread use in the paper industry.

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[31] M. J. Vittengl, *Paper Mill 61*, No. 1: 15–16, 20 (Jan. 1, 1938)
[32] A. R. Kemp, *Ind. Eng. Chem. 30*, No. 2: 154–158 (Feb., 1938)
[33] *Am. Dyestuff Reptr. 25*, No. 5: 109–111 (1936)

Chlorinated rubber is made by passing chlorine into a solution of natural crepe rubber until the rubber molecules are substantially saturated at the double bonds and some hydrogens are replaced. Commercial chlorinated rubber, which contains approximately 63 to 65% chlorine, is sold in the form of a white, amorphous powder. It is available in several different viscosities. Chlorinated rubber can be dissolved at high concentration in solvents, from which it produces transparent, glossy, and non-tacky films which are highly resistant to water, acids, and alkalies. Some of the solvents for chlorinated rubber are aromatic hydrocarbons, chlorinated hydrocarbons, esters, and aliphatic hydrocarbons. The film is brittle by itself, but plasticizers can be added for flexibility. Chlorinated rubber is compatible with alkyd resins, modified alkyds, coumarone-indene resins, dammar, and paraffin.

Another rubber derivative, known as cyclized rubber, is prepared by reacting natural rubber with strong acids or acid-forming salts, such as stannic chloride or chlorostannic acid. The final products range from rubbery materials to hard, brittle solids. Cyclized rubber has good heat-seal properties and excellent resistance to water vapor. It is soluble in a wide variety of solvents, including the aliphatic hydrocarbons, aromatic hydrocarbons, and the terpenes (see Ch. XXII). It is compatible with dammar, rosin, ester gum, and modified phenolics. It can be used in lacquers and hot-melt compositions.

Rubber hydrochloride is made by treating rubber with hydrochloric acid. Films of rubber hydrochloride are flexible, tough, transparent, and resistant to water and greases. However, the product is not widely used for paper coating because of its poor solubility and high viscosity in solvents. It is soluble in aromatic and chlorinated hydrocarbons, but is insoluble in ethers, esters, and alcohols. It is unsuited for hot melts because of its instability at high temperatures. It has been used to some extent in coatings where good heat sealing is necessary, and in paper laminates.

The treatment of rubber with strong acids in the presence of phenol produces thermoplastic derivatives of excellent adhesive properties. The products are soluble in benzene, toluene, and gasoline.

Synthetic Rubbers

Natural rubber has several serious disadvantages, one of which is its susceptibility to oxidation, which causes it to lose its flexibility after exposure to atmospheric oxygen. Certain metals (e.g., manganese and copper) promote this oxidation. Synthetic rubbers are not as susceptible to oxidation as natural rubber, and hence are preferred for certain uses. During World War II, synthetic rubbers became of great industrial importance, and today are being used in solvent form and as latices made by emulsion polymerization. Synthetic rubber latices are quite unstable unless protected with added protective colloids. For example, Nazarro[35] has shown that unstabilized synthetic rubber latex will be flocculated within three-quarters of an hour after zinc oxide is added, whereas, in the presence of 1% of an alkylolamine-fatty acid condensation product, flocculation time is increased to 1,200 hours.

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[34] I. Williams, *Ind. Eng. Chem. 29*, No. 2: 173–174 (Feb., 1937)

Among the types of synthetic rubber suitable for use in the paper industry are polychloroprene (neoprene), isobutylene polymers, isobutylene-diolefin polymers (Butyl rubber, GR-1), butadiene-styrene copolymers (Buna S-GRS, Pliolite, Latex 512K), and butadiene-acrylonitrile copolymers (Buna N-GRA, Chemigum 200, Hycar OR-25, Hycar OR-15).

Butadiene-styrene copolymers have proved to be one of the most satisfactory substitutes for natural rubber. They are soluble in ketones and esters, and are also available in emulsion form. A new polymer of the butadiene-styrene type which is suitable as a substitute for cyclized rubber is S-7 resin. This is offered as a 30% unmodified solution in toluene, or as a compounded material ready prepared for paper coating. The material is also available in latex form.[36] The S-7 resin is readily soluble in benzene, toluene, xylene, naphtha, and ketones. When aromatic solvents are used, the solution may be diluted as much as 50 to 75% by weight with cheap petroleum thinners. The product is compatible with waxes, modified phenolic resins, coumarone-indene resins, modified styrene resins, and ester gum. Butadiene-styrene copolymers can be made in different ratios of butadiene and styrene ranging from pure polybutadiene (a soft, weak rubber) to pure polystyrene (a hard, brittle resin). Increasing the styrene content increases the hardness, tensile strength, and stiffness, but decreases the elongation. GR-S rubber latex may contain styrene content up to 50%.

Isobutylene, obtained from cracked petroleum, can be polymerized to form a series of materials ranging from oily substances to rubber-like compounds. The outstanding characteristics of these polymers are toughness, chemical inertness, and low-temperature flexibility. The polymers are soluble in aliphatic and aromatic hydrocarbons, and also in some chlorinated hydrocarbons. They are compatible with paraffin, linseed oil, asphalt, hydrogenated coumarone-indene resins, terpene resins, and melamine-formaldehyde resins. They are suitable for use in pressure-sensitive adhesives, hot-melt coatings, and hot-melt adhesives. Styrene-isobutylene copolymers are also available commercially. These resins combine plastic and rubber-like properties. They are soluble in aliphatic, aromatic, and chlorinated hydrocarbons, and are compatible with wax. Butyl rubber is made by copolymerizing isobutylene with a diolefin (e.g., isoprene). This permits the cross linking of chains during vulcanization. Butyl rubber is soluble in carbon tetrachloride and slightly soluble in aliphatic and aromatic hydrocarbons. It is compatible with paraffin, linseed oil, alkyds, nitrocellulose, and some rosin derivatives. It is suitable for hot-melt coatings and laminating adhesives.

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[35] R. T. Nazarro, *Paper Trade J. 121*, No. 19: 90, 94 (Nov. 22, 1945)

[36] Pliolite Latex 170 sold by Goodyear Tire and Rubber Co., Inc., Akron, Ohio

Butadiene-acrylonitrile copolymers are soluble in ketones, xylol, cyclohexane, nitropropane, ethylene dichloride, chlorobenzene, butyl acetate, and 1-chloro-1-nitroethane. They are compatible with rosin, rosin derivatives, phenolics, nitrocellulose, rubber derivatives, and the polyvinyls. These polymers are available in solid and latex form. The latex contains dispersed particles having dimensions of 600 to 3000 A.[37]

The isobutene polymers constitute another class of synthetic rubber. These polymers are soluble in alcohols, esters, and ketones, and are compatible with paraffin. They can be used in hot melts and in adhesive formulations.

The polychloroprene polymers (neoprene) are made by converting acetylene to vinyl acetylene and then to chloroprene by reacting with hydrochloric acid. The products are soluble in benzene, trichloroethylene, methyl ethyl ketone, furane, toluene, ethylene dichloride, carbon tetrachloride, and coal tar naphtha. These polymers are not widely used in solvent form in the paper industry, but have found some use in latex form, where superior aging properties are desired. Neoprene latices are compatible with natural rubber latex and with some synthetic resin emulsions, especially rosin derivatives. They are incompatible with vinyl resins. The dispersed particles have a smaller particle size than those in natural rubber latex. Neoprene latex is available containing particles with a positive charge.

The olefin polysulfide polymers are prepared by the reaction of ethylene dichloride with sodium polysulfide. These polymers are characterized by outstanding resistance to aromatic and aliphatic hydrocarbons, as well as alcohols, esters, and ketones. They are, however, soluble in chlorinated hydrocarbons. The polymer has an undesirable odor.

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[37] D. M. Yost and W. H. Aiken, "The Effect of Certain Latex Variables in Beater Addition of Nitrile Rubber Latices." Paper presented at TAPPI Paper-Plastics Conference, Syracuse, N. Y. (Oct. 19-20, 1950).

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